



## Official Notice.

### DEFENCE OF THE REALM REGULATIONS.

An Order-in-Council, dated 7th September, further amends the "Defence of the Realm (Consolidation) Regulations, 1914." The following amendments in the Regulations are ordered:—

#### (SECTION 1.) REQUIREMENT OF DISCLOSURE OF PARTICULARS OF INVENTIONS, PROCESSES OF MANUFACTURE, ETC., RELATING TO WAR MATERIAL.

After regulation 8c the following regulation shall be inserted:—

"8cc. It shall be lawful for the Admiralty or Army Council or Minister of Munitions, with a view to the more efficient or increased production of war material, to require any person, to communicate to a person nominated for that purpose by the Admiralty, Army Council, or Minister of Munitions all such particulars as may be in his possession of any invention, or process or method of manufacture, or of any article manufactured or proposed to be manufactured, and to furnish drawings, models, or plans thereof, and to explain and demonstrate the same to such person, in all or any of its uses and workings; and if any person fails or neglects to comply with any such requirement he shall be guilty of an offence against these regulations; and if the requirement is addressed to a company, every director, manager, or officer of the company who fails or neglects to comply with such requirement shall also be guilty of an offence against these regulations.

"If any person, except as authorised by the Admiralty or Army Council or Minister of Munitions, discloses or makes use of any information obtained in consequence of any requirement made under this regulation or communicated to him by the person by whom it was so obtained, he shall be guilty of an offence against these regulations.

"No communication of an invention made in consequence of any requirement under this regulation, or the use thereof by any person authorised under this regulation to use it, shall prejudice any right of the inventor or owner thereof subsequently to apply for or obtain a patent for the invention."

### Edinburgh Section.

Meeting held at Edinburgh, on Wednesday, May 17th, 1916.

PROF. JAMES WALKER IN THE CHAIR.

#### SOME ASPECTS OF THE SYNTHESIS OF CAOUTCHOUC.

BY B. D. W. LUFF, F.I.C.

The synthesis of caoutchouc was recorded long before any very definite ideas were formulated as to its constitution. Pure caoutchouc is a hydrocarbon having the empirical formula  $C_5H_8$ ; its molecular weight, however, cannot be ascertained by means at present available, owing to the fact that it is a colloid. Moreover, the number of simple derivatives which may be obtained is

extremely limited and these, being chiefly amorphous and almost impossible to obtain in a pure condition, afford very little insight into the nature of the parent substance. The most readily prepared is the bromide,  $C_5H_7Br$ , a white amorphous solid formed by treating caoutchouc with bromine in chloroform solution; it is, however, almost impossible to obtain a specimen which approximates sufficiently closely to the empirical formula, to be considered as pure. Perhaps the most interesting derivative is the diozonide, which can be prepared by passing ozone into a chloroform solution of caoutchouc; on evaporation a vitreous solid is obtained, melting at  $50^\circ C$ . Harries (Ber., 1905, 38, p. 1195) found that this had a molecular weight corresponding to the formula  $C_{10}H_{16}O_8$ . On hydrolysis this yields equimolecular proportions of levulinic aldehyde and levulinic aldehyde peroxide, the latter subsequently breaking up into levulinic acid and hydrogen peroxide. Hydrochloric acid and oxides of nitrogen also combine with caoutchouc forming compounds which are more or less ill-defined and need not be discussed here.

More interesting results, however, are obtained on submitting caoutchouc to destructive distillation. As far back as 1833 a patent was granted to Barnard for the invention of "a solvent not hitherto used in the arts" which was obtained by distilling rubber from an iron retort; this oil could be used to dissolve caoutchouc itself, resins, fatty bodies, etc., and, moreover, could be used as an illuminant. The work was subsequently taken up on more scientific lines by various investigators, including Dalton, Liebig, Himly, A. Bouchardat, and Gregory, their results being embodied in various publications issued between 1835 and 1840, but in all cases their efforts were more or less disjointed.

The most systematic attempt to isolate and examine the various products present in the crude distillate was made by Greville Williams in 1860. He obtained (1) a liquid boiling at  $37^\circ C$ . to which he gave the name "Isoprene"—the molecular formula of this body was found to be  $C_5H_8$ ; (2) a large proportion of a hydrocarbon boiling at  $170^\circ$ – $173^\circ C$ , which was identical with a body previously obtained by Himly, and called caoutchine—the molecular formula of this was  $C_{10}H_{16}$ , and it may be noted that it has since been proved to be dipentene; (3) a fraction boiling above  $300^\circ$  to which he gave the name "Heveene."

Some years later, in 1879, Gustave Bouchardat, son of A. Bouchardat, undertook a detailed investigation of isoprene, in the course of which he examined the action of hydrochloric acid; he noted that an addition product was formed but under certain conditions the action of the acid resulted in the formation of a solid mass, not containing chlorine, but having in fact the same percentage composition as the isoprene itself. In describing this body he says "it possesses the elasticity and other properties of rubber itself. It is insoluble in alcohol swells up in ether and also in carbon bisulphide in which it dissolves after the fashion of natural rubber." Moreover, he noted that on distillation it yielded the same hydrocarbons as in the case of the natural product.

This, then, was an important step in the synthesis of caoutchouc; in fact, in order to make this complete, all that was necessary was to prepare isoprene, a comparatively simple hydrocarbon, from elementary materials; at that time the only source of isoprene was rubber itself.

Although Bouchardat regarded the product he had obtained as identical with natural rubber, yet the fact that it was elastic and behaved in a similar manner towards solvents did not suffice to establish definitely the relationship existing between them.

Bouchardat's results received confirmation in 1882 at the hands of Tilden (Chem. News, 1882, 46, 120) who observed the polymerisation of isoprene when treated with nitrosyl chloride, a reagent which he had used in connection with work on terpenes. In discussing isoprene he remarked that one of the chief characteristics of this body was its conversion into true caoutchouc or indiarubber when brought into contact with certain chemical reagents; he pointed out that this was of great practical interest as, if isoprene could be obtained from some other and more accessible source, the synthetical production of rubber could be accomplished. Two years later Tilden succeeded in obtaining isoprene by passing the vapours of turpentine through a hot tube, the yield, however, being very small in proportion to the amount taken; nevertheless the solution of the problem at any rate from a commercial point of view appeared to be in sight as the initial material was fairly abundant and the cost not excessive.

The outcome of the work of these two investigators was that the caoutchouc molecule was shown to be formed by the union of a number of molecules of isoprene, i.e., it was a polymer of this body, and moreover this union or polymerisation could be brought about by treating the isoprene with suitable reagents.

To them must be given the major share of the credit for laying the foundation of the numerous processes since suggested for preparing synthetic rubber. The importance of their observations will be apparent when we consider that this method of polymerising a simple hydrocarbon is at present the only one by which the complex rubber molecule may be said to have been reproduced. Their work affords a very good illustration of the value of making careful note of changes occurring during a reaction; what organic chemist has not at some time or another succeeded in obtaining, instead of the crystalline solid he had hoped for, an uninviting plastic mass which was promptly discarded as of no consequence? However, Bouchardat and Tilden had in their favour the knowledge that the isoprene which they used had been obtained from rubber itself, so that the identity of their product with this body would the more readily suggest itself.

Subsequently Wallach (Annalen, 1887, 238, 88) observed that isoprene underwent polymerisation on exposure to light with production of a rubber-like mass. Tilden (Chem. News, 1892, 65, 265) also drew attention to this phenomenon and at the same time recorded the fact that the material obtained in this manner could be vulcanised with sulphur in the usual way, this pointing to a close relationship existing between the synthetic and the natural material.

Some idea of the quantitative nature of the polymerisation may be gathered from the statement by Weber (this Journal, 1894, 13, 11) to the effect that from 300 grms. of isoprene, after a period of 9 months, 211 grms. of caoutchouc was obtained.

The synthesis of isoprene and as a corollary that of caoutchouc was accomplished by Euler in 1897 (Ber., 1897, 30, 1989) and his work together with that of Ipatiew (J. prakt. Chem., 1897, 55, 4) established the constitution of this body, showing it to be  $\beta$ -methyldivinyl,  $\text{CH}_2\text{:C}(\text{CH}_3)\text{CH:CH}_2$ . This supported the view entertained by Tilden some time previously.

The auto-polymerisation of isoprene was confirmed later by Pickles (Trans. Chem. Soc., 1910, 97, 1085); in this case the change was not complete after upwards of three years. The product possessed a certain amount of elasticity but was

not equal to Para rubber, resembling rather that obtained from immature trees; the comparison, it may be noted, was based on unvulcanised samples. Pickles, furthermore, prepared derivatives with the aid of bromine and oxides of nitrogen, in each case obtaining bodies apparently identical with those resulting from the employment of natural rubber.

The nature of the polymerisation of the simple isoprene molecule to the caoutchouc complex was also discussed by this worker, whose views are as nearly as possible in accordance with observed facts. The union of the  $\text{C}_5\text{H}_8$  groups is held to be a chemical one, caoutchouc being represented by a chain of an indefinite number of these units connected at the ends to form a ring. This conception, which is perhaps the simplest of the many put forward, has been contested by Harries and others, but in the meantime may be accepted as it does not involve the assumption of molecular aggregation of an unnecessarily vague character.

With the synthesis of isoprene in 1897, the problem of the synthetical production of caoutchouc, at least from an academic point of view, could be regarded as solved. For some time, however, no serious attempt was made to put it on a satisfactory commercial basis.

One of the first methods which attracted attention was that suggested by Heinemann in 1907, which consisted in passing a mixture of acetylene, ethylene, and methyl chloride through a hot tube when isoprene should result.

$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_4 + \text{CH}_3\text{Cl} = \text{CH}_2\text{:C}(\text{CH}_3)\text{CH:CH}_2 + \text{HCl}$ . This reaction, however plausible it might seem, did not appear to take place as desired, with the result that the method was abandoned; it is interesting, however, as being the first instance in which an industrial concern had endeavoured to make the synthesis a commercial success.

Another type of process which at this time received treatment at the hands of a number of workers was that in which, following the lines indicated by Tilden, turpentine was submitted to "cracking" processes. This line of work, which at first sight seemed fairly promising, was ultimately abandoned as supplies of the initial material were becoming somewhat limited and the tendency was for prices to rise; in any case, the yield of isoprene was never satisfactory.

In 1909, owing no doubt to the rapid rise in the price of rubber, the problem was attacked in a systematic manner in this country by a group of chemists which included among others Perkin, Fernbach, Weizmann, and Matthews; in Germany, too, the Bayer and the Badische Companies had taken the matter up and from this time onward an enormous number of processes have been outlined which, at any rate, may be said to be alive with possibilities.

To give anything like a detailed account of these would be outside the scope of this paper, but it will suffice to give types illustrative of the varied ways by which the desired end may be attained. It must be clearly understood, however, that the instances quoted are merely by way of illustration and in no way to be considered as likely to lead to better results than could be obtained in the case of most other methods.

In 1884 Tilden suggested that not only isoprene but its homologues should be capable of polymerisation in a similar manner. This was indeed found to be the case, as subsequent investigators showed that many unsaturated hydrocarbons containing conjugated double bonds exhibited this property, the products thus formed varying from resinous masses to rubber-like bodies. Chief among them may be mentioned butadiene (or erythrene),  $\text{CH}_2\text{:CH:CH:CH}_2$ , and dimethylbutadiene,  $\text{CH}_3\text{:C}(\text{CH}_3)\text{C}(\text{CH}_3)\text{:CH}_2$ . It is not surprising then to find these compounds forming

the basis of methods for obtaining synthetic caoutchoucs.

In considering the materials available, as the starting points for suggested syntheses, it would be as well to confine our attention to those of which the supply is fairly abundant. Among these coal tar at once suggests itself, and indeed a process has been worked out starting from *p*-cresol. This is first reduced by the Sabatier method, the product oxidised to  $\beta$ -methyladipic acid, and by elimination of the carboxyl groups, together with two atoms of hydrogen, isoprene is obtained. In a similar manner, starting with phenol, butadiene can be prepared; the number of stages necessary to complete the reaction, however, renders the process of little value.

The low-boiling fractions obtained in petroleum distillation have also been suggested as the starting points for obtaining isoprene. The normal and iso-pentanes which are present are converted into dihalogen derivatives and from these two molecules of HCl eliminated. The chief difficulty in processes of this type is in arriving at the desired dihalogenide and many methods have been suggested with a view to surmounting this obstacle.

From starch isoprene may be prepared in a variety of ways; most noteworthy is the method described by Perkin (this Journal, 1912, 621) which consists in bringing about fermentation in such a manner that amyl alcohols are produced in much greater proportion than is usually the case; these are converted into dichloro-derivatives and two molecules of HCl split off by means of soda-lime, isoprene being thus produced. Butadiene can be prepared in a similar manner from butyl alcohol.

From starch again ethyl alcohol may be obtained, and according to Ostromyslenski (this Journal, 1916, 69) if this is passed along with a little air over heated copper gauze a proportion of the alcohol is oxidised to acetaldehyde; the mixture of aldehyde and alcohol is then passed over heated alumina whereupon water is eliminated and butadiene produced.

$\text{CH}_3\text{CHO} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2 = \text{CH} \cdot \text{CH} = \text{CH}_2 + 2\text{H}_2\text{O}$ . This process is certainly suggestive and appeals to one by its very simplicity, but the success; will naturally depend on the yield of butadiene as a general rule pyrogenetic reactions of this type do not take place in one direction only. It is worthy of note that Ostromyslenski (*loc. cit.*) has quite recently published a series of papers dealing with new methods for preparing these hydrocarbons; these are remarkable if for nothing else than the exhaustive consideration which he has given to the subject, as an instance of which may be cited one paper in which he describes no less than 29 new methods for preparing butadiene.

Cellulose has also been suggested as raw material for preparing isoprene; a method has recently been worked out for obtaining levulinic acid in considerable quantity by submitting sawdust to the hydrolytic action of dilute acids under pressure. With the aid of phosphorus trisulphide the acid so obtained is converted into methylthiophene and by passing this over heated copper along with a stream of hydrogen, isoprene is formed,  $\text{H}_2\text{S}$  being eliminated.

These instances then may be taken as typical of the many processes put forward as being likely to lead to the commercial preparation of isoprene and other closely related bodies.

The production of the necessary unsaturated hydrocarbon is however merely the first stage in the synthesis of caoutchouc, the next step being to bring about polymerisation by some means.

At the outset it was generally recognised that agents hitherto employed in experiments on a

laboratory scale did not give at all satisfactory yields of rubber and the need for a more efficient method was evident. One of the most promising was that proposed by Harries in 1910 (this Journal, 1910, 502) which consisted in heating isoprene in a sealed tube with glacial acetic acid; subsequently the same worker announced that better results could be obtained by the use of sodium, the polymerisation to caoutchouc taking place almost quantitatively in the cold. Curiously enough this same agent had already been patented in this country by Matthews and Strange, the former having made the discovery in 1910; the patent however had not been disclosed, so that evidently it was an instance of different investigators arriving at the same result independently of each other. Harries prepared and described two series of rubbers resulting from the polymerisation of butadiene, isoprene, etc., on the one hand with sodium as the condensing agent, and on the other hand using acetic acid. The products obtained by the use of sodium, although resembling rubber in so far as their physical properties were concerned, did not behave similarly when submitted to chemical treatment. The acetic acid products presented a closer analogy from a chemical standpoint but were inferior physically.

It is interesting to note in passing that Greville Williams in 1860 distilled his isoprene over sodium, but most probably the two bodies would not be left in contact for any considerable time, at any rate not long enough for any appreciable polymerisation to take place.

Without venturing to give any definite opinion as to the future developments in connection with the many processes hitherto evolved for producing synthetic rubber, the present position may be put briefly as follows:—

There is no doubt that caoutchouc-like bodies have been prepared by means similar to those outlined above; as to whether these can be regarded as true caoutchouc is a matter of doubt. It will be understood that on account of the colloidal nature of this body the question cannot be settled by determining such physical characteristics as would serve to identify a crystalline solid such as camphor. In the case of a body such as the latter the specific properties which render it of interest can be directly attributed to a well defined molecular structure, the reproduction of which by whatever means ensures possession of these properties. In the case of caoutchouc, however, this cannot be brought about with certainty. Indeed, many of the proposed methods do not purport to give a product chemically identical with the natural material. In the case of the polymerisation of butadiene ( $\text{C}_4\text{H}_6$ ), it is manifestly impossible to obtain a body having an empirical formula  $\text{C}_5\text{H}_8$ , although physically the resulting mass is perhaps the most satisfactory of any obtained up to the present.

Harries (this Journal, 1912, p. 733) holds the view that caoutchouc obtained from isoprene with the aid of acetic acid is identical with that occurring in nature, basing this assertion on a study of the ozonides. That derived from the synthetic material is said to give on hydrolysis levulinic acid and levulinic aldehyde only, the reaction proceeding with the same velocity as in the case of the natural derivative. On the other hand Steimmig (this Journal, 1914, p. 268) dissents from this opinion, the results of his experiments on the hydrolysis leading him to the conclusion that there is present, in addition, a body produced by the asymmetric polymerisation of isoprene. Harries however maintains his original attitude and attributes Steimmig's results to the use of impure isoprene.

The synthetic caoutchouc obtained by polymerising isoprene in the presence of sodium, however, is not identical with the natural product as neither levulinic acid nor levulinic aldehyde is formed on submitting the ozonide to hydrolysis.

It might be urged that the chemical characteristics are of relatively little importance if the material fulfils all the needs of the manufacturer, and this is undoubtedly the correct view to take. Up to the present, however, the quantities of synthetic rubber produced have been so small as not to admit of a comparison being made with the natural material on anything like a satisfactory scale. The rubber manufacturer knows too well that a substance which might truthfully be called a "tough elastic mass" or "caoutchouc-like body" need not necessarily be as good in every way as the product of the plantations in the East.

A glance through one or two specifications to which various rubber articles must conform would quickly convince the reader that a product destined to replace caoutchouc for all purposes must possess properties of a very varied character.

Even if a synthetic body were obtained which could be said to compare favourably with the natural article, the price would obviously become a determining factor in the chance of success; it is here that an industrial process would encounter almost insuperable difficulties. At the time when chemists began to turn their attention towards synthetic rubber the price of this commodity was abnormally high, reaching as much as 12s. 6d. per lb. in 1910. Since then, however, there has been a steady fall, reaching as low as 2s. 4d. per lb. in 1915. This is accounted for by the plantations coming into bearing, the products thereof occupying a very prominent place in the world's markets. The recent growth of the plantation industry, and the very different conditions which a synthetic product has now to face compared with those obtaining in quite recent years, can be seen at a glance from the following tables:—

*Plantations—area under rubber.*

	Ceylon.	Malaya.
1901 .. ..	2,500 acres	nil
1912 .. ..	230,000 "	621,621 acres

*Tons of plantation rubber exported.*

	Ceylon.	Malaya.
1904 .. ..	35 tons	nil
1912 .. ..	6,697 "	18,956 tons

*World's supply of plantation rubber.*

1912 .. ..	28,500 tons
1915 .. ..	98,000 "

The rapid strides which have been made in the cultivation of rubber will thus be evident, and as there is every prospect of the yields increasing for some time to come this is bound to react on the price, and it is generally assumed that unless a synthetic product can be put on the market at about 1s. 3d. per lb. there is little hope of the natural material being superseded.

As chemists, perhaps, it would be gratifying to know that another triumph had been won in the industrial field, but whatever the outcome may be, it is well to remember that the chief factor militating against success is the result of scientific energy expended in other directions, that is to say, in raising the product of the plantation to the highest pitch of perfection.

# SOME NOTES ON THE RAW MATERIALS USED BY THE RUBBER MANUFACTURER.

BY B. D. PORRITT, M.SC., F.I.C.

The many varied applications which have been found for rubber in the arts may be attributed in the first place to the remarkable alteration in

its physical properties which occurs when this substance is mixed with sulphur and heated, and secondly to the further modifications which can be effected by the incorporation of various mineral and organic substances. The first process is known as "vulcanisation" and the second as "compounding."

Were it not for the discovery and development of these processes the rubber industry would never have reached its present importance, and, instead of uses innumerable, the technical application of rubber would probably have been limited to the manufacture of waterproof garments and similar goods.

First of all, rubber itself, and the changes it undergoes when treated with sulphur and vulcanising agents, may be considered, and subsequently some of the other ingredients which are added by the manufacturer in order further to modify the physical and other properties of his products will be dealt with briefly.

Raw rubber is often far from a clean substance when it reaches the manufacturer, and usually requires washing and drying prior to use. The moisture and impurities removed by this process have been known on occasion to amount to as much as 60% for some dirty varieties of wild African rubber, but the average for the supplies of uncultivated raw material would be nearer half this figure.

Owing to the rapid development of the plantation industry many inferior types of wild rubber have dropped out of the market, and in place of the almost endless variety available some eight years ago, the manufacturer of to-day is mainly concerned with the various grades of wild Para and cultivated *Hevea* rubber, for which the combined washing and drying losses are about 20% and 1% respectively.

This change in the supply of the primary raw material obviously represents a very important simplification for the rubber manufacturer, both from the point of view of purchasing and uniformity of factory running.

Even after washing and drying, good quality rubber is not a chemically pure substance, since it still contains, besides caoutchouc, a small quantity of resin, some nitrogenous and other organic substances, together with a small amount of mineral matter. For instance, an average sample of plantation sheet, after washing and air drying for four weeks, will contain about 94.5% of caoutchouc, the difference being made up by about 0.25% of moisture, 0.25% of ash, 2.5% resins, and about 2.5% insoluble nitrogenous and other organic impurities.

In addition to the variations which exist in the amounts of the non-caoutchouc constituents present, it is found that the caoutchouc in different rubbers is itself not always identical in physical properties, and in dealing with different varieties of rubber considerable variation will be found in the resistance to oxidation, the temperature of softening, the viscosity of solutions, and the amount of mechanical working required in preparing the material for factory use. Such variations must be attributed to the fact that caoutchouc is a colloid.

Exposure to light, mechanical working, heating, etc., considerably modify the properties of raw rubber without any corresponding chemical change being detectable,\* and, owing to the inapplicability of any of the usual tests which serve as criteria of purity for crystalline organic compounds, it is impossible to determine whether chemically purified caoutchouc is a simple substance or a mixture. It is interesting to notice in this connection that almost every worker in this field has experienced difficulty in preparing purified material

\* Harries, *Annalen*, 1911, **383**, 157.

free from oxygen, and that Caspari,\* by means of petroleum ether, has separated the caoutchouc from wild and cultivated *Hevea* into two varieties, differing in their physical properties and behaviour towards solvents.

Those unfamiliar with the rubber industry might be inclined to ask why the manufacturer is satisfied generally merely to remove the gross mechanical impurities without further chemical purification. The removal of the resins and nitrogenous constituents representing the chief impurities would, however, be an exceedingly difficult operation on the technical scale, and would in addition result in an inferior product. The former constituent is found to enhance greatly the resistance of the caoutchouc to oxidation, to which under certain conditions it is somewhat prone,† and moreover appears to play a considerable part in the process of vulcanisation, litharge in its absence being inoperative as an accelerator. It has for some time been known that the nitrogenous constituents also facilitate vulcanisation, but these substances have recently attracted increased attention as a result of some investigations carried out by the Laboratory of the Agricultural Department of the Federated Malay States,‡ which would indicate that the variation in the rate of vulcanisation, which constitutes the chief defect of the plantation rubber, is probably to be attributed to irregular changes which take place in these proteid constituents in consequence of variations in the process of separating and drying the coagulum from the latex. The fact, however, remains that rubber, and plantation rubber in particular, cannot be regarded as fulfilling at present one of the essentials of an ideal raw material in that it is not uniform in quality. Variation in vulcanisation properties, which is the chief defect, will inevitably result in variations in strength under the conditions of uniform treatment necessary during the manufacture of rubber goods on a large scale, when it is evidently impracticable to modify the conditions of vulcanisation to suit each individual consignment of rubber. Technical experience would indicate, moreover, that the cultivated product is somewhat inferior to Para rubber for the preparation of solutions, and also in its resistance to the repeated application of stresses such as are experienced by articles such as catapult cord. Investigations which have as object the production of a uniform plantation product are beset with both scientific and geographical difficulties, due to the complexity of the problems involved and the wide separation of the producer and consumer. Recent publications, however, manifest substantial progress towards this goal. They testify, moreover, that those responsible for the future of one of our youngest and most successful commercial enterprises, which in the course of a few years has made the British Empire the largest rubber producer in the world, are fully alive to the necessity for continuous progress and the need for scientific research.§

At the same time co-ordination between the several agencies responsible for research in this field, with the elimination of jealousy and overlapping, is evidently desirable if rapid progress is to be made in the production of the uniform plantation product so important in the interests of the consumer.

The remarkable changes which are effected in the properties of rubber by the addition of sulphur and heating can now be considered.

If two mixtures, the one containing about 95% of rubber and 5% of sulphur, the other 85% and

35% respectively, are heated in steam, the former for about 2½–3 hours at 50 lb. pressure and the latter for a considerably longer period at a higher pressure, striking changes will be found to have taken place in their physical qualities, and they will besides present a marked contrast in appearance. The sample with the low sulphur content on comparison with the untreated material will be found to be little altered in appearance, but enormously improved in strength and resilience.

Further, it will have become insoluble at ordinary temperatures in the usual solvents for rubber, and a proportion of the added sulphur will be found to have become firmly combined with the caoutchouc. The second sample will have been transformed into a hard, jet black material, totally different in its properties from the original yellow plastic mixture of rubber and sulphur.

These examples illustrate the two distinct branches of rubber manufacture—"soft rubber" and "hard rubber." The latter is known also as "vulcanite" or "ebonite," and the process by which these changes are effected is termed "vulcanisation" or "curing." The formation of "hard rubber" can be explained by the assumption that an addition compound  $(C_5H_8S)_x$  is formed by the unsaturated caoutchouc and the sulphur. This empirical formula corresponds to a combined sulphur content of 32%, which is in accordance with observed facts. Whether other molecular changes accompany this reaction it is impossible to determine in the absence of information regarding the molecular weights and constitutions of the initial and final products.

The nature of "soft cured" rubber is less readily explained, and in spite of a considerable amount of research work during recent years, it is still a subject of discussion.

Satisfactory vulcanisation may be effected by the combination of from 1.5 to 4.5% of sulphur, depending on the nature of the other ingredients present; these figures do not correspond with the formation of any definite caoutchouc-sulphur compound, though it cannot be assumed that the sulphur has combined uniformly, and possibly there may be present varying quantities of a definite caoutchouc-sulphur compound or compounds dissolved in unchanged caoutchouc. If vulcanised rubber consists of such a mixture its resolution into the several constituents has not as yet been effected. It would seem probable that, in addition to the combination of sulphur, some polymerisation change may take place in the caoutchouc with the formation of a substance of higher molecular aggregation insoluble in solvents.

The polymerising action of sodium on isoprene and butadiene is interesting in this connection; but it is noteworthy that vulcanised rubber "depolymerised" during the process of "reclaiming" does not become soluble once more in solvents.

The remarkable effect produced by this small addition of sulphur was discovered by Goodyear in 1839. It is therefore surprising to find that, in 1916, sulphur is still almost exclusively employed for the purpose of vulcanisation.

No satisfactory explanation has as yet been advanced to account for this property, possessed apparently by sulphur alone of the elements, or for the fact that this action can be accelerated by the presence of litharge and basic substances, and that, in the absence of litharge, a certain amount of pressure seems necessary for the action to take place satisfactorily.

At various times compounds, such as hypochlorites, iodine, and polysulphides, have been proposed as vulcanising agents, but have found at the most only limited technical application.

According to the latest suggestion of this kind a large number of aromatic nitro-compounds are

\* Caspari, this J., 1913, 104.

† Percey, this J., 1912, 1103.

‡ Eaton and Grantham, this J., 1915, 898.

§ For contrary opinion see H. E. Armstrong, this J., 1916, 601.

efficient substitutes for sulphur in the process of vulcanisation.\*

It has been found that dinitrobenzene, one of the substances named, is quite inoperative as a vulcanising agent,† and simultaneous work in this laboratory‡ employing pure 1-methyl-2,4,6-trinitrobenzene confirms the foregoing observation; this latter substance acts neither as a vulcaniser nor an accelerator, but rather as an oxidising agent, the rubber being markedly deteriorated on heating when appreciable quantities of the nitro-compound are admixed.

Apart from sulphur one substance only, and that a sulphur compound, has found general application for the purpose of vulcanisation, the use of sulphur monochloride at ordinary temperatures for this purpose having been patented by Parkes in 1846. The vulcanisation of rubber may, therefore, be effected by one of two general methods—the “hot cure” process, in which sulphur and heat are the agents, and the “cold cure” process just mentioned.

There are three modifications of the former method in general use.

(1) The “steam heat” process can be used for textile and other goods on which the rubber coating is comparatively thin, the material being suitably protected from the deposition of moisture and subjected to the action of steam under pressure. The tendency of the uncombined sulphur to effloresce or “bloom up” on the surface renders this process inapplicable when brightly coloured goods are desired. A modification of this method has been described recently in which the heating is carried out in an indifferent gas under pressure.§

(2) The “dry heat” process also employed for lightly rubbered articles, especially shoes, differs from the previous instance in vulcanisation being effected at ordinary pressure in large hot-air chambers heated by steam pipes. The presence of litharge in addition to sulphur is essential to the success of this process and, owing to the consequent formation of lead sulphide, articles vulcanised in this way are always black. The open heating, however, results in the volatilisation of the greater part of the free sulphur, so that a permanent dead black finish is secured.

(3) The “press cure” process is employed for heavy articles, such as buffers and motor tyres, which are vulcanised in moulds placed in heated hydraulic presses.

The “cold cure” process is rapid and results in a material possessing a soft velvety finish. It permits the production of brilliantly pigmented articles which will not “bloom” but which are generally somewhat deficient in permanence. This method, which is suitable only for lightly coated goods, can be carried out either by dipping in a dilute solution of sulphur chloride in carbon bisulphide or by exposure to the vapour in a large chamber. Whichever method is used, an after-treatment with ammonia must follow to neutralise any acid formed by the action of moisture on the excess sulphur chloride.

Incorrect vulcanisation probably is responsible for as much trouble in the factory as is caused by inferior or defective raw materials. Not only will it result in defective physical qualities, but the material will be liable to oxidise or “perish” in the course of a few weeks, if the treatment has been unduly severe.

The conditions and duration of heating to ensure satisfactory vulcanisation will depend upon the nature of the ingredients and the proportion of each in the mixing. It is therefore of the utmost importance that the rubber manufacturer should

employ uniform raw materials, and should submit all factory mixings to careful physical tests in the laboratory in order to determine the correct conditions of vulcanisation, judged by strength and durability, before undertaking the manufacture of goods for sale.

The many other fillers employed by manufacturers, apart from rubber and sulphur, remain for brief consideration. These sometimes are spoken of as “drugs” in the trade. This metaphor is very appropriate since they are materials which, while valuable in skilled hands, may become deleterious when misapplied. It has been said,\* “If it had never occurred to any one to mix extraneous substances with rubber, it is safe to say that the industry as we know it would be inconceivable; rubber manufacture would have expanded perhaps in volume, but hardly in scope, beyond its boundaries of pre-vulcanisation times. In unvulcanised rubber we have one material, in soft cured rubber a second, and in ebonite a third; but by admitting compounding ingredients we gain innumerable new materials. Moreover, the lowering of prices thus achieved has done much to widen the market for rubber goods.”

In making such additions, the manufacturer may have any of the following objects in view:—(1) Mechanical properties, such as stiffness, toughness, etc. (2) Chemical or physical properties, for example, indifference to acids and dielectric resistance. (3) Colour. (4) Duration of vulcanisation. (5) Cost. These “compounding” ingredients may be divided into two classes, organic substances such as reclaimed rubber, rubber substitute, and bitumen; and mineral compounds, for example, zinc oxide, barytes, and whiting.

It is unnecessary to consider exhaustively the merits and defects of the many different fillers employed by rubber manufacturers, and it will suffice to refer to some of the more important. It might be mentioned in passing, however, that compounds of copper appear to exert a highly prejudicial influence on the durability of rubber goods, and must be avoided carefully for this reason.† A “pure” vulcanised rubber, on account of its extensibility and softness, would be unsuitable for many purposes involving abrasion or compression. It is therefore necessary to incorporate a suitable proportion of mineral matter when rubber is needed for mechanical uses, and zinc oxide and magnesia are the fillers generally favoured by manufacturers for this purpose. The conditions to be satisfied by an eraser are in direct contrast to the foregoing requirements, and, instead of being tough and resistant to abrasion, the material must be flexible and friable. These qualities can be secured by the employment of a large proportion of “white rubber substitute,” prepared by acting on rape oil with sulphur monochloride. This, when the goods are dark in colour, can be replaced by a “brown substitute” resulting from the action of sulphur on vegetable oil at a high temperature.

The choice of pigments for the production of coloured articles depends to a considerable extent on the method of vulcanisation selected.

When vulcanisation by heat is necessary the number of pigments which are at the same time cheap and permanent is somewhat limited, the ones generally used being antimony sulphide, yellow arsenic sulphide, zinc chromate, green oxide of chromium, ultramarine, and lamp-black. The cold cure process permits a selection being made from a much wider range of colours, including many brilliant permanent dyes and lake pigments.

\* Ostromyski, *this J.*, 1916, 59.

† Stevens, *Le Caoutchouc et la Gutta Percha*, 1916, 8880.

‡ The author in conjunction with Mr. W. G. Martin.

§ *India Rubber World*, 1916, 883.

\* Caspari, “*India Rubber Laboratory Practice*,” p. 87.

† Thomson and Lewis, *this J.*, 1891, 712.

Dewar, *this J.*, 1891, 71.

The question of accelerators for the hot vulcanisation process may now be considered. These are important for three reasons. In the first place, their use ensures a larger output from the vulcanising plant, or permits the employment of lower temperatures; secondly, they provide a means whereby the correct vulcanisation conditions of two different mixings used in conjunction may be made identical, as, for example, the tube and cover of a hose, and finally by their use the addition of sulphur may be somewhat reduced with a view to minimising "blooming." Litharge is the most effective of these substances, but lime, magnesia, and certain basic organic compounds\* possess the same property in a lesser degree, and can be employed when colour or other considerations render the use of litharge inadmissible.

The production of satisfactory rubber goods at moderate prices for the many purposes which do not require high mechanical strength has been greatly assisted by the discovery and development of the acid and alkali processes for reclaiming waste rubber. By means of reduction to a fine state of division and chemical treatment followed by washing, it is found possible to remove the textile impurities generally present in rubber waste. The cleaned material can subsequently be restored to a plastic condition by heating in steam under pressure, and the product may after drying be employed either partially or wholly to replace rubber in mixings, which can be vulcanised in the usual manner.

It is noteworthy that up to the present all the various processes having as their object the removal of combined sulphur and the regeneration of the caoutchouc in a soluble form have met with no success, since the combined sulphur appears to be retained tenaciously. Reclaimed rubber, therefore, prepared from vulcanised waste, will be insoluble in rubber solvents, and will contain unchanged the greater proportion of the original fillers, since the methods of preparation have as object merely the restoration of plasticity.

This necessarily superficial sketch of the materials used by the rubber manufacturer would be incomplete without reference to the large amounts of textiles which are used in conjunction with rubber in such articles as motor and cycle tyres, hose, waterproofs, and the like. Such fabrics, usually cotton, must possess the requisite strength, be unaffected by vulcanisation, and be free from any dressing likely to affect the durability of the rubber.

From what has gone before it will be clear that the successful manufacture of rubber goods depends on the observance of three conditions, namely, uniform supplies, suitable mixings, and correct vulcanisation. Failure on the part of the manufacturer to comply with any of these essentials is certain to result sooner or later in serious trouble, which may be either immediate or appear after the goods have been distributed to the consumer.

An efficient chemical and physical laboratory must therefore be regarded as an essential in a rubber works. The preparation of suitable mixings and the physical testing necessary to ascertain the correct conditions of vulcanisation will demand a special section in the department equipped with a miniature factory milling and vulcanising plant, together with all the necessary testing machines for rubber and textiles.

The chemical uniformity of the supplies of raw materials and the investigation of problems in the factory requiring scientific assistance may be left for attention to the chemical section of the works laboratory.

It will remain nevertheless for the research chemist to raise the manufacture of rubber from a somewhat empirical operation, however well controlled it may be by physical and chemical tests, to one which is based on scientific principles. The problems presented by colloid chemistry are difficult of solution and the progress is slow; but until the constitution of rubber and the mechanism of the vulcanisation process are more clearly understood the rubber industry cannot be said to be on a sound scientific basis.

## Communication.

### THE DETERIORATION OF LEATHER USED IN GAS METERS.

BY M. C. LAMB.

In the early part of 1913 the author was consulted by the South Metropolitan Gas Company, and at their request commenced a somewhat elaborate and lengthy investigation with the view to elucidate the cause or causes which were responsible for the rapid deterioration of the leather employed in the construction of gas meters.

The author now places on record the results of this investigation, so far as it has progressed, as a contribution to the general discussion on the important subject of "The Life of Gas Meters"; a preliminary report of a Joint Committee appointed by the Institution of Gas Engineers and the Society of British Gas Industries has recently been published (see this J., 1916, 824).

As is well known to gas engineers there has, of recent years, been a gradually increasing tendency on the part of gas meters to require repairing on account of either partial or complete breakdown of the mechanism of the diaphragm used as a measuring instrument for the amount of gas passing, thus interfering with the correct recording of the quantity of gas consumed.

The major portion of the complaints were apparently traceable to the leather used, either in the form of a complete diaphragm, or perhaps more generally used to form the connecting bellows of two diaphragms made of tin plate, the leather having apparently undergone some form of deterioration, thereby losing its necessary property of providing a gas-tight medium.

*Meter leather requirements.*—The hitherto recognised requirements of the meter manufacturer, as understood by those three or four firms of leather manufacturers specialising in the manufacture of "Meter leathers," may be summarised as follows:—

(1) The leather, with one exception, that general usage has demanded has been the so-called "Persian" sheepskin, a native-tanned East India sheepskin. The selection of this particular class of skin was no doubt due to the fact that this leather, on account of its close texture and compact fibre structure, was less liable to porosity, and hence was considered more suitable for the purpose than domestic sheepskins, which possess a more open texture and porous character, and are naturally greasy.

(2) The leather, when dressed, must be supple, be free from excessive natural fat, and free from stretch; it is a necessary stipulation that the skins should be specially selected for freedom from holes.

(3) The substance of the leather is to a great extent determined by the size of the diaphragm upon which it is intended to be used—thin substance skins, e.g., 0.4 to 0.5 mm. for 6-light meters, to from 1.0 to 1.5 mm. for the larger sizes.

(4) In the majority of cases the meter manufacturer stipulates that the grain of the leather should be removed by buffing, the object of this

\* Dittmar, *Le Caoutchouc et la Gutta-Percha*, 1915, p. 8681.



apparently being to make it softer and to increase its power of absorbing the oil and graphite mixture used as a finishing dressing; the buffing produces a surface which is capable of retaining a greater proportion of the dressing than in the case when the grain has not been so removed.

(5) The exception mentioned above (1), so far as the author is aware, only refers to one particular meter manufacturer in Great Britain, and is therefore in the nature of an individual experiment. The leather used is a split sheepskin of British tannage, known as a skiver, i.e., the grain side of a sheepskin; it is of thin substance, has little tensile strength, and is liable, unless extreme care is taken in the selection, to be entirely unsuitable on account of its tendency to possess natural perforations known as "pinholes," due to the natural growth of the skin. It has been stated to be satisfactory in use, but in the author's opinion it is not suitable for general adoption on account of its somewhat irregular physical character and its low tensile strength, though the latter factor does not play so important a part as one might anticipate without a full knowledge of the internal working of the meter leather when in use, and its method of attachment. The fact of its employment is interesting, however, as showing that, with the one exception, every British meter manufacturer has adhered to the use of the E.I. sheepskin, and though this was not considered satisfactory, particularly during recent years, apparently no other kind of leather has been tested with the object of finding a better substitute, or the experiments have resulted in failure.

*General investigation of causes of deterioration.*—The investigations of the author were in the first place directed to the leathers employed and their condition after being in use for varying periods, as ascertained by examining the leather and diaphragms removed from a very considerable number of meters of many makes, returned to the repair shop of the South Metropolitan Gas Company.

This examination revealed the fact that in almost every instance the perforation of the meter leather was in the majority of cases examined in a line drawn parallel to the periphery of the metallic diaphragm to which the leather was attached, the extent of the perforation varying from  $\frac{1}{4}$  inch to, in a great many cases, five or six inches. The leather, on examination after having been freed from the remains of the graphite and oil dressing, whilst being sound and unaffected in the centre of the leather strip, was hard and perished where it had come in direct contact with either the metallic band fastening the leather to the diaphragm, or with the diaphragm itself. In every case examined, the leather where it had perished and become hard was also discoloured, and was in the majority of cases practically black. In one or two instances a narrow strip of leather had been placed in direct contact with the metal diaphragm, and under the meter leather, to act as a cushion when the meter leather was fixed by hemp cord or string; this strip of leather, which was protected from direct contact with the gas, had, in every case examined, become completely perished.

Subsequent analytical investigations showed that at the points mentioned the deterioration of the leather had undoubtedly been caused by iron, which had converted the tannin into a tannate of iron; this, by continuous oxidation and reduction, made the leather hard and caused it to disintegrate and perish. The amount of iron found was in some examples as great as 0.3% (Fe).

*Methods of attachment of diaphragms.*—Attention was next paid to the various methods of attaching the leather to the diaphragms as adopted by the various makers. These consisted of either (a) attachment by means of steel bands, most

commonly covered to protect the band, either with linen tape or leather, or (b) attachment with several coils of hemp cord drawn tightly round the edge of the metal diaphragm, a cushion being made of a thin strip of leather as stated above, to produce a tight joint.

In the few cases examined where the metal band was covered with leather, it was found that the leather in contact with the metal band had also entirely perished and become black and brittle.

The author ascertained that some manufacturers, with a view to the production of a tight joint, used various adhesives to embed the leather when the band was tightened up, so as to close up and make gas-tight any small crevices or openings that might otherwise result. A number of these were examined, e.g., flour paste, mixtures of resin and tallow, paraffin wax and tallow, and buck tallow. A sample of flour paste examined was found to contain an appreciable percentage of alum. Such a mixture must be unhesitatingly condemned, as owing to the free sulphuric acid liberated it dissolves the metallic band and thereby hastens the deterioration of the leather by transference of the resulting iron salt to the leather.

A mixture of ordinary tallow having, as is usual, a high "acid value," due to the condition of rancidity, must also be condemned for the purpose. Mixtures containing resin are also unsuitable.

The most suitable materials for the purpose, in the opinion of the author, if it is considered necessary to embed the leather in this way, are either paraffin wax, rendered sufficiently plastic by mixing with a small quantity of vaseline, or pure buck tallow, which must not possess a high acid value.

One of the earliest changes made in the repair shop of the South Metropolitan Gas Co., and which has since been retained after some three years' experience, was the substitution of an aluminium band for the steel band attachment. The employment of an embedding agent has been discontinued, as being unnecessary when the fitting was carefully performed.

It is of the utmost importance that the leather should be quite dry before it is fixed to the meter, and the stock of leather should be stored in a dry atmosphere; otherwise the moisture in the leather will quickly cause pitting of the tinned surface of the metal diaphragm at the points of contact with the leather, with consequent exposure of the iron surface.

*Oil used in dressing.*—Samples of the oil used by the meter manufacturers for mixing with graphite to produce a leather dressing were examined. Almond oil has long been employed for this purpose and has peculiarly suitable properties.

The oil used for the manufacture of the dressing should be a non-volatile, non-drying oil, and must remain liquid at low temperatures; it must also be an oil which does not become rancid and has a low "acid value."

Almond oil possesses all these properties. Other suitable oils fulfilling the necessary qualifications are peach kernel oil and apricot kernel oil; these are often used to adulterate almond oil, being cheaper, but for the purpose under review they are just as suitable.

Sulphonated oils are quite unsuitable either for use in the making of the graphite dressing or in the treatment of the leather.

It has been stated that manufacturers of meters in the United States do not employ any oil dressing in the leathers used. The advantage of the dressing as a protective covering against any injurious chemical impurities of the gas is obvious if reasonable care is taken that the oil used is the most suitable obtainable. The graphite acts as a filling agent, closing up the interstices of the

fibres, and tends to produce a more perfect gas-tight medium. The use of petroleum jelly (vaseline) to replace almond oil has not been adopted, but it appears to the author to possess advantages that render it particularly suitable.

**Experiments with meter liquids.**—Several samples of the liquid condensate from a number of gas meters were examined. A number of samples were found to contain small amounts of ammonia and ammonium salts, compounds of cyanogen, and a fairly high percentage of inorganic non-volatile salts was found, and salts of iron and tin were present in comparatively large amounts. To ascertain the effect of the condensates on meter leathers, samples of different leathers were immersed in samples of liquids removed from meters in which the original leathers had been adversely affected. The results obtained were of a negative character; in every case the condensate had no appreciable effect when used as above, though the experiments were prolonged over six months.

An interesting experiment, which threw some light on the causes of deterioration, consisted of binding strips of leather round pieces of the metallic band used for attaching the meter leather to the diaphragm, and immersing these in meter liquids. The leather in every case, whether the steel band was protected or not with linen strips, was deteriorated and rendered brittle; the deterioration at those parts in contact with the metal was most pronounced, but also extended but to a lesser degree to those portions which were not in direct contact.

This experiment confirms to an appreciable extent the deduction formed on examination of a large number of leathers that had been removed from meters and which had probably perished, as mentioned above, owing to the corrosive action of the acid and ammonia constituents of the gas on the metal band.

**New leathers for gas meters.**—Experiments were made with several leathers of different tannage to those ordinarily employed as mentioned above. Leathers of vegetable tannage are particularly susceptible to deterioration by the action of acid fumes and of alkaline gases; leathers tanned with mineral tannage agents are not so injuriously affected. In the light of this fact meter leathers were prepared of chrome tannage, also alum tannage, and semi-chrome tannage, which latter consisted of a vegetable tanned East India (Persian) sheepskin from which the greater portion of the original vegetable tannage had been removed by treatment with weak alkaline salts, and replaced by retanning with basic chromium sulphate or chloride.

Leathers of these three different tannages were placed in meters, and to obtain a result as quickly as possible several meters were fixed in various parts of the South Metropolitan Gas Works where they were continuously in service; some few meters fitted with the experimental leathers were also placed on the ordinary circuit. At varying periods some of the meters were disconnected and the contents examined.

**Alum tanned leather.**—The alum tanned leather underwent considerable deterioration, and after a short period became hard and possessed the appearance of being undertanned, probably owing to the action of the ammoniacal gases. Previous experiments, made by immersing the leather for a lengthy period in meter liquids, had indicated the unsuitability of the leather, the meter liquid being found to possess a solvent action upon the tannage.

**Chrome tanned leather.**—On the other hand it was found that the sample of chrome tanned leather was quite unaffected, remaining soft and supple and apparently in as good a condition as when first enclosed in the meter.

**Semi-chrome leather.**—The behaviour of a well-chromed semi-chrome leather, so far as could be ascertained by the somewhat severe tests to which the samples of leather were subjected, was equally encouraging as the fully chrome tanned leather. Samples removed from the test meters after two years' trial showed no signs of deterioration whatever.

Samples of both the chrome and semi-chrome leathers were analysed before and after the experiment. The results of the chemical tests showed practically no change in the leather, as given below:—

	Chrome leather.		Semi-chrome leather.	
	Before.	After.	Before.	After.
Mineral ash ....	per cent. 5.7	per cent. 5.9	per cent. 3.25	per cent. 3.3
Chromic oxide ..	3.0	3.0	2.1	2.15

The following tensile strength tests were made:—

Chrome leather.		Semi-chrome leather.	
Mean of 4 tests of strips 1 inch wide by 2 inches long.		Before.	
Before treatment.	21.4	Before.	21.0
After.	20.7	After.	21.5

A careful comparative microscopical examination of sections of each of the leathers showed that the samples had undergone no deterioration of the leather fibres.

In view of the fact that the experiments had shown, so far as could be ascertained in the limited time over which the tests had been made, that the semi-chrome East India tanned leather was undoubtedly superior to the ordinary East India (Persian) in general use, it was decided to adopt this leather provisionally for general repair work and in the manufacture of meters constructed by the South Metropolitan Gas Company.

The following specification was eventually adopted with a view to obtaining from various contractors a leather that contained a sufficient chrome content to ensure that the leather had been properly retanned with the basic chromic salt, and having in view the most suitable treatment for the purpose of providing a leather that the experiments indicated to be the most promising.

*Specification for the supply of leather intended for use in gas meters.*

*Semi-chrome East India ("Persian") Sheep.*

#### *Material.*

1. The skins are to be dressed from a good quality East Indian tanned "Persian" sheepskin of naturally "dry" tannage.
2. The goods to be selected of as near as possible the requisite substance in the crust condition, in order to avoid the necessity of materially reducing the substance by shaving all over the skin.
3. The goods to be reasonably free from grain defects and "tick" and from flaying defects; the skins to be free from holes.

#### *Dressing.*

1. The skins to be prepared by lightly stripping with borax, washing, and retanning with basic chromium sulphate or basic chromium chloride in sufficient quantity to give the required chromium content given below (2).
2. The leather to contain 2.0% to 2.5% of chromic oxide on the dry weight of finished leather.
3. The leather to be neutralised after retanning.
4. The fat-liquoring to be done with neatfoot oil and neutral soda soap, using an amount

equivalent to 3% oil and 2% soap on the dry finished leather.

5. The leather to be staked, fluffed, and lightly buffed on the grain side, except when expressly stipulated that buffing is not to be done.

6. The goods to be soft full supple leather, and free from any inclination to hardness.

One of the advantages in favour of the adoption of this leather was that it could be supplied by any firm of leather dressers ordinarily engaged in the dressing and finishing of East India tannages.

Subsequent experience has inclined towards the adoption of real chrome leather made from a domestic or New Zealand lamb skin, for use upon the smaller size meters, but retaining the semi-chrome tanned East India sheep for larger size meters. Real chrome leather in the majority of cases was found to be too soft and inclined to bagginess when employed upon large size meters, a defect which is conducive to incorrect registration. Semi-chrome E.I. sheep of 1 to 2 mm. thickness possesses, when properly dressed, the right amount of suppleness without any inclination to be so soft as to be liable to sag when used as the bellows of the meter.

The specification which has been provisionally adopted for real chrome lamb leather is as follows:—

#### *Chrome Leather.*

##### *Material.*

1. The skins to be tanned from a domestic lamb skin or New Zealand pickled lamb pelt of good quality, of 6 to 8 square feet area.
2. The goods to be specially selected for freedom from cockle, and be reasonably free from butcher cuts, holes, and other defects.
3. The skins to be selected of as near as possible the required substance in order to avoid the necessity of shaving.

##### *Tannage and Dressing.*

1. The goods to be tanned by the chrome process, and to contain a minimum of 3% chromic oxide, calculated on the dry (degreased) finished leather.
2. The goods after tanning to be neutralised and afterwards fat-liquored with a minimum of 2% neatsfoot oil and 1% soda soap on the dry finished leather weight.
3. No glycerine or other substance of a hygroscopic nature to be applied to the goods.
4. The goods to be staked, strained, and fluffed on the flesh side, and delivered in the original undyed blue colour.
5. The skins to be supple, fully tanned, well nourished leather, and to be free from any tendency to hardness.

It is extremely satisfactory to report that since the adoption of the semi-chrome leather for use upon all meters of the South Metropolitan Gas Company, which change was made on the author's suggestion as far back as July 1913, not one meter fitted with these leathers has been received by the repair shop for renewal of the leather, and in all the numerous cases which have been examined, including the original experiment and tests made on meters in continuous service, no deterioration of the leather has been observable.

Whilst the author does not claim that the substitution of the two leathers above referred to is the final answer to the question under discussion, the practical result shows that the adoption is at any rate one step in the right direction.

The resistance of chrome leather (and of leather semi-chromed to such a degree that it possesses practically the whole of the essential properties of the full chrome product) to the action of small traces of acid, and of alkaline gases, was thoroughly

investigated by the author some years ago,\* in continuation of the investigations of the special Society of Arts Committee on the Deterioration of Leathers for Bookbinding, published in 1901.

It is also now a well known fact that the life of chrome tanned belting leathers used for the transmission of power in chemical and other works, where they are subjected to various chemical gases, is much greater than is the case with ordinary vegetable tanned leather, and also longer than is the case of the majority of cotton and other fibre belts.

In the recent report,† made by Dr. Lessing to the Joint Committee representing the Society of British Gas Industries and the Institution of Gas Engineers, reference has been made to the investigations of the Society of Arts Committee on the Deterioration of Bookbinding Leathers, referred to above.

Dr. Lessing gives details of analyses of 21 samples of leathers used for diaphragms in which the percentage of acid (in terms of sulphuric acid) varied from 0.64% to 1.37% in leathers that had not been used. These results are entirely contradictory to the author's experience.

As above referred to, the ordinary meter leathers are made from sheepskins tanned in East India, chiefly by native tanners in a comparatively small way of business. The term "Persian" applied to these goods does not indicate the source of origin, and is only a trade description that originated many years ago, when an importer having discovered these goods in India was desirous of eliminating competition for their purchase, and in order to mislead his trade rivals called them Persian sheepskins, which resulted in keeping the source of supply secret for some time; the original route for East Indian shipping was by way of the Persian Gulf.

No mineral acid is used by the native tanner in the manufacture of these goods, and in a lengthy experience of these goods the author has not known a single case where the leather has been found to contain sulphuric or other mineral acid in the original condition as imported.

The author can also vouch for the fact that the three principal leather manufacturers specialising in the manufacture of leather for meter diaphragms do not use sulphuric acid in the dressing of these particular goods. The use of sulphuric acid for clearing and improving the ground colour of East Indian and other tannages preparatory to dyeing bright and fancy shades of colour, was quite common before the investigation of the Society of Arts Committee, and resulted in the rapid deterioration of these leathers when used for bookbinding; this practice has now ceased upon these leathers, following the report in question. It has never been common in the case of meter leathers.

With reference to the statement made in Dr. Lessing's report that the presence of decomposition products of leather was found in the non-volatile residues obtained from meter liquids, from which he infers that there has been solvent action of the gas and meter liquids upon the leather diaphragm, the author would point out that some small amount of leather substance is invariably present in all meter liquids. This does not necessarily originate by reason of any solvent action of the gases or the meter liquid, but is often due to the fact that the leather on account of its having been subjected to mechanical attrition on both sides on an emery wheel, has a fine velvety nap surface, and if not carefully brushed before being cut up, introduces a quantity of leather dust into the meter which subsequently finds its way into the meter liquid. The samples of meter liquids

\* J. Soc. Dyers and Col., 1906, 24, 160; this J., 1908, 820.  
† See this J., 1916, 824.

examined by the author have had, as above stated, little solvent action upon pieces of leather that have been immersed in them for long periods.

The above results of the investigation are not considered by the author to be final, but, as stated in the opening paragraph, to be a contribution to the discussion on the subject. Further experimental work is in progress, and the author hopes to be able to communicate any interesting results dealing with this important industrial problem, in due course.

The author desires to take this opportunity of expressing his thanks to the Chairman of the South Metropolitan Gas Company (Dr. Carpenter) for granting him permission to publish the results of his investigations.

Leathersellers' Technical College,  
Tower Bridge Road,  
London, S.E.

### British Association.

Section B.—Newcastle-on-Tyne, 1916.

#### ADDRESS TO THE CHEMICAL SECTION.

BY PROFESSOR G. G. HENDERSON, D.SC., LL.D., F.R.S.,  
President of the Section.

(Abstract.)

The period which has elapsed since 1885 has witnessed remarkable progress in every branch of pure and applied chemistry. Whilst the study of the compounds of carbon has been pursued with unflagging energy and success, it has no longer so largely monopolised the activities of investigators. Interest in the other elements, which had been to some extent neglected on account of the fascinations of carbon, has been revived with the happiest results.

The more purely scientific side of our science can claim no monopoly in progress, for applied chemistry, in every department, has likewise advanced with giant strides, mainly of course through the application of the results of scientific research to industrial purposes. Many of the more striking results in the field of modern chemical industry have been obtained by taking advantage of the powers we now possess to carry out operations economically both at very high and at very low temperatures, and by the employment on the manufacturing scale of electrolytic and catalytic methods of production. Thanks largely to the invention of the dynamo, the technologist is now able to utilise electrical energy both for the production of high temperatures in the different types of electric furnace and for electrolytic processes of the most varied description. Among the operations carried out with the help of the electric furnace may be mentioned the manufacture of graphite, silicon, and phosphorus; of chromium and other metals; of carbides, silicides, and nitrides; and the smelting and refining of iron and steel. Calcium carbide claims a prominent place in the list, in the first place because of the ease with which it yields acetylene, which is not only used as an illuminant, and, in the oxy-acetylene burner, as a means of producing a temperature so high that the cutting and welding of steel is now a comparatively simple matter, but also promises to serve as the starting-point for the industrial synthesis of acetaldehyde and many other valuable organic compounds. Moreover, calcium carbide is readily converted in the electric furnace into calcium cyanamide, which is employed as an efficient fertiliser in place of sodium nitrate or

ammonium sulphate, and as a source of ammonia and of alkali cyanides. Among the silicides carborundum is increasingly used as an abrasive and a refractory material, and calcium silicide, which is now a commercial product, forms a constituent of some blasting explosives. The Serpek process for the preparation of alumina and ammonia, by the formation of aluminium nitride from bauxite in the electric furnace and its subsequent decomposition by caustic soda, should also be mentioned. Further, the electric furnace has made possible the manufacture of silica apparatus of all kinds, both for the laboratory and the works, and of alundum ware, also used for operations at high temperature. Finally, the first step in the manufacture of nitric acid and of nitrites from air, now in operation on a very large scale, is the combustion of nitrogen in the electric arc.

In other industrial operations the high temperature which is necessary is obtained by the help of the oxy-hydrogen or the oxy-acetylene flame, the former being used, amongst other purposes, in a small but I believe profitable industry, the manufacture of synthetic rubies, sapphires, and spinels. Also, within a comparatively recent period, advantage has been taken of the characteristic properties of aluminium, now obtainable at a moderate price, in the various operations classed under the heading aluminothermy, the most important being the reduction of refractory metallic oxides, although, of course, thermite is useful for the production of high temperatures locally.

The modern methods of liquefying gases, which have been developed within the period under review, have rendered possible research work of absorbing interest on the effect of very low temperatures on the properties and chemical activity of many substances, and have been applied, for instance, in separating from one another the members of the argon family, and in obtaining ozone in a state of practical purity. Moreover, industrial applications of these methods are not lacking, amongst which I may mention the separation of nitrogen and oxygen from air, and of hydrogen from water-gas—processes which have helped to make these elements available for economic use on the large scale.

Electrolytic methods are now extensively employed in the manufacture of both inorganic and organic substances, and older processes are being displaced by these modern rivals in steadily increasing number. It is sufficient to refer to the preparation of sodium, magnesium, calcium, and aluminium, by electrolysis of fused compounds of these metals; the refining of iron, copper, silver, and gold; the extraction of gold and nickel from solution; the recovery of tin from waste tin-plate; the preparation of caustic alkalis (and simultaneously of chlorine), of hypochlorites, chlorates, and perchlorates, of hydrosulphites, of permanganates and ferricyanides, of persulphates and percarbonates; the regeneration of chromic acid from chromium salts; the preparation of hydrogen and oxygen. As regards organic compounds, we find chiefly in use electrolytic methods of reduction, which are specially effective in the case of many nitro compounds, and of oxidation, as for instance the conversion of anthracene into anthraquinone. At the same time a number of other compounds, for example iodoform, are also prepared electrolytically.

Within recent years there have been great advances in the application of catalytic methods to industrial purposes. Some processes of this class have, of course, been in use for a considerable time, for example the Deacon chlorine process and the contact method for the manufacture of sulphuric acid, whilst the preparation of phthalic anhydride (largely used in the synthesis of indigo and other dyestuffs), by the oxidation of naphtha-

lene with sulphuric acid with the assistance of mercuric sulphate as catalyst, is no novelty. More recent are the contact methods of obtaining ammonia by the direct combination of nitrogen and hydrogen, and of oxidising ammonia to nitric acid—both of which are said to be in operation on a very large scale in Germany. The catalytic action of metals, particularly nickel and copper, is utilised in processes of hydrogenation—for example, the hardening of fats, and of dehydrogenation, as in the preparation of acetaldehyde from alcohol, and such metallic oxides as alumina and thoria can be used for processes of dehydration—*e.g.*, the preparation of ethylene or of ether from alcohol. Other catalysts employed in industrial processes are titanous chloride in electrolytic reductions and cerous sulphate in electrolytic oxidations of carbon compounds, gelatin in the preparation of hydrazine from ammonia, sodium in the synthesis of rubber, etc.

Other advances in manufacturing chemistry include the preparation of a number of the rarer elements and their compounds, which were hardly known thirty years ago, but which now find commercial applications. Included in this category are titanium, vanadium, tungsten, and tantalum, now used in metallurgy or for electric-lamp filaments; thoria and ceria in the form of mantles for incandescent lamps; pyrophoric alloys of cerium and other metals; zirconia, which appears to be a most valuable refractory material; and compounds of radium and of mesothorium, for medical use as well as for research. Hydrogen, together with oxygen and nitrogen, are in demand for synthetic purposes, and the first also for lighter-than-air craft. Ozone is considerably used for sterilising water and as an oxidising agent, for example in the preparation of vanillin from isocugenol, and hydrogen peroxide, now obtainable very pure in concentrated solution, and the peroxides of a number of the metals are also utilised in many different ways. The per-acids—perboric, percarbonic, and persulphuric—or their salts are employed for oxidising and bleaching purposes, and sodium hydrosulphite is much in demand as a reducing agent—*e.g.*, in dyeing with indigo. Hydroxylamine and hydrazine are used in considerable quantity, and the manufacture of cyanides by one or other of the modern methods has become quite an important industry, mainly owing to the use of the alkali salts in the cyanide process of gold extraction. Those remarkable compounds the metallic carbonyls have been investigated, and nickel carbonyl is employed on the commercial scale in the extraction of the metal. Fine chemicals for analysis and research are now supplied, as a matter of course, in a state of purity rarely attained a quarter of a century ago.

In the organic chemical industry similar continued progress is to be noted. Accessions are constantly being made to the already enormous list of synthetic dyes, not only by the addition of new members to existing groups, but also by the discovery of entirely new classes of tinctorial compounds; natural indigo seems doomed to share the fate of alizarin from madder, and to be ousted by synthetic indigo, of which, moreover, a number of useful derivatives are also made. Synthetic drugs of all kinds—antipyrine and phenacetin, sulphonal and veronal, novocain and  $\beta$ -eucaine, salol and aspirin, piperazine and adrenaline, atoxyl and salvarsan—are produced in large quantities, as also are many synthetic perfumes and flavouring materials, such as ionone, heliotropine, and vanillin. Cellulose in the form of artificial silk is much used as a new textile material, synthetic camphor is on the market, synthetic rubber is said to be produced in considerable quantity; and the manufacture of materials for photographic work and of organic compounds for research purposes is no small part

of the industry. However, it would serve no useful purpose to extend this catalogue, which might be done almost indefinitely.

British chemists are entitled to regard with satisfaction the part which they have taken in the development of scientific chemistry during the last three decades, as in the past, but with respect to the progress of industrial chemistry it must be regretfully admitted that, except in isolated cases, we have failed to keep pace with our competitors. Consider a single example. Although there still remain in South America considerable deposits of sodium nitrate which can be worked at a profit, it is clear that sooner or later other sources of nitric acid must be made available. The synthetic production of nitric acid from the air is now a commercial success; several different processes are in operation abroad, and Germany is reported to be quite independent of outside supplies. Electrical energy, upon the cost of which the success of the process largely depends, can be produced in this country at least as cheaply as in Germany, and yet we have done nothing in the matter, unless we count as something the appointment of a committee to consider possibilities. This case is only too typical of many others. A number of different causes have contributed to bring about this state of affairs, and the responsibility for it is assigned by some to the Government, by others to the chemical manufacturers, and by still others to the professors of chemistry. I think, however, it will be generally admitted that the root of the matter is to be found in the general ignorance of and indifference to the methods and results of scientific work which characterises the people of this country.

I believe that a brighter day is dawning, and that, if only we rise to the occasion *now*, chemistry in this country will attain the position of importance which is its due. The Government has taken a most significant step in advance by appointing an Advisory Council for Scientific and Industrial Research and providing it with funds (see this J., 1915, 783; 1916, 424, 912).

The adoption by the Government of the recommendations made by a Sub-Committee of the Advisory Committee to the Board of Trade on Commercial Intelligence (see this J., 1916, 279) would go far to establish British chemical industry on a secure basis, and would undoubtedly lead to the expansion of already existing branches and the establishment of new ones. Meanwhile, the Australian Government has set an example which might be followed with great advantage, and their admirable scheme (this J., 1916, 440) is more comprehensive and more generous than that of our Government, but it could be rivalled without much difficulty. We already possess an important asset in the National Physical Laboratory, and there now exists the Advisory Council with its extensive powers and duties. What is lacking in our scheme, so far as chemistry is concerned, could be made good, firstly, by providing the Advisory Council with much larger funds, and, secondly, by the establishment of a National Chemical Laboratory—an institute for research in pure and applied chemistry—or by assisting the development of research departments in our universities and technical colleges (as is now being done in America), or, better still, by moving in both directions.

It has been suggested by Dr. Forster that the State could render assistance to chemical industry in another way, namely, by the formation of a Chemical Intelligence Department of the Board of Trade, which should be concerned with technical, commercial, and educational questions bearing upon the industry (see this J., 1915, 763, 1173). This proposal, which has been widely discussed and on the whole very favourably received by chemists, has much to recommend it. The principal objec-

tions which have been raised are based upon the fear that the proposed Department, however energetic and enterprising it might be at the start, would soon be so helplessly gagged and bound down by departmental red tape as to become of little or no service. This danger, however, could be obviated to a great extent by the institution of a strong Advisory Committee, representative of and elected by the Societies concerned with the different branches of chemistry, which would keep closely in touch with the Chemical Intelligence Department on the one hand and with the industry on the other, and which would act as adviser of the permanent scientific staff of the Department. There is, I fear, little chance of seeing Dr. Forster's proposal carried into effect unless all the Societies concerned move actively and unitedly in the matter; they must do the pioneer work and must submit a definite scheme to the Government, if the desired result is to be attained. In the not improbable contingency that the Board of Trade will decline to take action, I trust that the scheme for the establishment of an Information Bureau—on lines similar to but somewhat less wide-reaching than those which I have just indicated—which has been under the careful consideration of the Council of the Society of Chemical Industry, will be vigorously prosecuted. Difficulties, chiefly financial, stand in the way, but these are not insuperable, especially if the sympathy and support of the Government can be enlisted.

Unless the conditions and methods which have ruled in the past are greatly altered it is hardly possible to hope that the future prospects of our chemical industry will be bright; it is essential that the representatives of the industry should organise themselves in their own interest and co-operate in fighting the common enemy. More than ever is this the case when, as we are informed, three different groups of German producers of dyes, drugs, and fine chemicals, who own seven large factories, have formed a combination with a capital of more than £11,000,000, and with other assets of very great value in the shape of scientific, technical, and financial efficiency. Hence it is eminently satisfactory to be able to record the active progress of a movement, originated by the Chemical Society, which has culminated in the formation of an Association of British Chemical Manufacturers (see this J., 1916, 561). The main objects of the Association are to promote co-operation between British chemical manufacturers; to act as a medium for placing before the Government and Government officials the views of manufacturers upon matters affecting the chemical industry; to develop technical organisation and promote industrial research; to keep in touch with the progress of chemical knowledge and to facilitate the development of new British industries and the extension of existing ones; and to encourage the sympathetic association of British manufacturers with the various universities and technical colleges.

Needless to say, the progress of this important movement will be assisted by everyone who is interested, either directly or indirectly, in the welfare of our chemical industry, and, moreover, the support of the scientific societies will not be lacking, for, as the result of a conference convened by the President and Council of the Royal Society, a Conjoint Board of Scientific Societies has been constituted, for the furtherance of the following objects:—Promoting the co-operation of those interested in pure or applied science; supplying a means whereby scientific opinion may find effective expression on matters relating to science, industry, and education; taking such action as may be necessary to promote the application of science to our industries and to the service of the nation; and discussing scientific questions in which international co-operation seems advisable.

In an Address given to the Society of Chemical Industry last year (this J., 1915, 747), I indicated another way in which chemical manufacturers can help themselves and at the same time promote the interests of chemistry in this country. In the United States of America individual manufacturers, or associations of manufacturers, have shown themselves ready to take up the scheme originated by the late Professor Duncan for the institution of industrial research scholarships tenable at the universities or technical colleges, and the results obtained after ten years' experience of the working of this practical method of promoting co-operation between science and industry have more than justified the anticipations of its originator. The scheme is worthy of adoption on many grounds, of which the chief are that it provides definite subjects for technical research to young chemists qualified for such work, that it usually leads to positions in factories for chemists who have proved their capacity through the work done while holding scholarships, and that it reacts for good on the profession generally, by bringing about that more intimate intercourse between teachers and manufacturers which is so much to be desired.

In this connection the recent foundation of the Willard Gibbs Chair of research in pure chemistry at the University of Pittsburgh is extremely significant, for it shows that even in such a purely industrial community as Pittsburgh it is recognised that the most pressing need of the day is the endowment of chemical research and the creation of research professorships. Mr. A. P. Fleming, who recently made a tour of inspection of research laboratories in the United States, points to the amount of work done by individual firms and the increased provision now being made for research in universities and technical institutions. He reports that at the present time there are upwards of fifty corporations having research laboratories, costing annually from £20,000 to £100,000 for maintenance, and states that "some of the most striking features of the research work in America are the lavish manner in which the laboratories have been planned, which in many cases enables large scale operations to be carried out in order to determine the best possible methods of manufacturing any commodity developed or discovered in the laboratories; the increasing attention given in the research laboratories to pure science investigation, this being, in my opinion, the most important phase of industrial research; and the absorption of men who have proven their capacity for industrial research in such places as the Mellon Institute, the Bureau of Standards, etc., by the various industries in which they have taken scientific interest." It is evidently the view of American manufacturers that industrial research can be made to pay for itself, and that to equip and maintain research laboratories is an excellent investment.

It cannot be too often reiterated that no branch of chemical industry can afford to stand still, for there is no finality in manufacturing processes; all are capable of improvement, and for this, as well as for the discovery and the application of new processes, the services of the trained chemist are essential. Hence the training of chemists for industrial work is a matter of supreme importance. Perhaps it is too much to expect that practice in research will be made an indispensable qualification for the ordinary degree; failing this, and indeed in every case, promising students should be encouraged, by the award of research scholarships, to continue their studies for a period of at least two years after taking the B.Sc. degree, and to devote that time to research work which would qualify for a higher degree. In this connection an excellent object-lesson is at hand, for the output of research work from the Scottish Universities has very greatly increased since the scheme of the

Carnegie Trust for the institution of research scholarships has come into operation. Thanks to these scholarships, numbers of capable young graduates, who otherwise for the most part would have had to seek paid employment as soon as their degree courses were completed, have been enabled to devote two or more years to research work.

On the whole, there is not much fault to be found with the training for chemists supplied by the universities and technical colleges, but there is still room for improvements which could and would be carried out if it were not that the scientific departments of these institutions are as a rule hampered by lack of funds. Hence no opportunity should be lost of impressing upon the Government the necessity for increasing the grants to the scientific departments of our higher teaching institutions, and for the provision of research scholarships. It is much to be desired also that wealthy men in this country should take an example from America and acquire more generally the habit of devoting some part of their means to the endowment of higher education. The private donations for science and education made in the United States during the last forty-three years amount to the magnificent sum of £117,000,000, and recently the average annual benefactions for educational purposes total nearly £6,000,000. Of course there are few, if any, of the universities and colleges in this country which are not deeply indebted to the foresight and generosity of private benefactors, but the lavish scale on which funds are provided in America leads to a certain feeling of admiring envy.

After all, the chief difficulty which confronts those who are eager for progress in educational matters is that so many of our most famous schools are still conducted on mediæval lines, in the sense that the "education" administered is almost wholly classical. Consequently, "though science enters into every part of modern life, and scientific method is necessary for success in all undertakings, the affairs of the country are in the hands of legislators who not only have little or no acquaintance with the fundamental facts and principles signified by these aspects of knowledge, but also do not understand how such matters can be used to strengthen and develop the State. Our administrative officials are also mostly under the same disabilities, on account of their want of a scientific training. They are educated at schools where science can receive little encouragement, and they do not take up scientific subjects in the examinations for the Civil Service, because marks can be much more easily obtained by attention to Latin and Greek; and the result of it all is that science is usually treated with indifference, often with contempt, and rarely with intelligent appreciation by the statesmen and members of the public services whose decisions and acts largely determine the country's welfare. The defects of a system which places the chief power of an organisation which needs understanding of science in every department in the hands of people who have not received any training in scientific subjects or methods are obvious."\* The remedy is also obvious.

Here, again, the prospects are now brighter than ever before, because the warnings and appeals of men of science have at last, and after many years, begun to bear fruit, or perhaps it would be more correct to say the lessons of the war have begun to make an impression on the powers that be. Within the last few weeks it has been intimated that the Government, giving ear to what has been uttered, incessantly and almost *ad nauseam*, with regard to British neglect of science, propose to appoint a committee to inquire into the position of science in our national system of education,

especially in universities and secondary schools. The duty of the committee will be to advise the authorities how to promote the advancement of pure science, and also the interests of trade, industries, and professions dependent on the application of science, bearing in mind the needs of what is described as a liberal education. It is stated that the committee will include scientific men in whom the country will have confidence, some of those who appreciate the application of science to commerce and industry, and some who are able from general experience to correlate scientific teaching with education as a whole. I am sure that we may look forward with confidence to the recommendations of such a committee, and we shall hope, for the sake of our country, that their recommendations will be adopted and put in force with the least possible delay.

## Institute of Metals.

September, 1916.

### THE DEVELOPMENT OF THE SPELTER INDUSTRY.

BY E. A. SMITH.

(Abstract.)

*Historical.* In 1830 the total production of spelter in Europe was less than 5000 tons; in 1840 it was a little more than 17,000 tons; and in 1870 it had grown to 128,289 tons (Germany 55,744, Belgium 45,745, Great Britain 15,000 tons). The annual production in the United States was at this time 4500 tons. The enormous increase in the rate of production and in the demand for zinc during the past fifty years is shown in the following table:—

Year.	European production.	American production.	World's production.	World's consumption.
	In long tons, 2240 lb.			
1870	128,000	4,500	133,000	
1880	207,000	21,000	228,000	236,000
1890	—	—	343,000	345,000
1900	310,000	58,000	368,000	474,000
1910	557,000	247,000	804,000	820,000
1913	663,000	315,000	982,000	997,000

The most important smelting centres contributing to the world's supply of zinc are Silesia, Westphalia, and Belgium, on the Continent, Swansea, in England, Illinois, Kansas, and New Jersey in the United States. Japan appears to produce about enough to supply her own demands.

The status of the world's zinc industry, prior to the war, is well shown in the following tables, which give the figures for the production and consumption of spelter in all the principal countries for ten years ending 1913, and also the average price in the London market.

*The spelter convention.* Before the war spelter reduction plants were in excess of the world's requirements, and the output was therefore controlled by a Spelter Convention to maintain the price. Out of the total world's production of zinc of 957,000 long tons in 1912, nearly one-third (345,000 tons) was controlled by the German Syndicate (associated German and Belgium makers), and nearly 571,000 tons by the International Syndicate (British and certain Belgian and French producers). *Ores of zinc.* Formerly calamine was the most important ore but at the present time zinc blende is the chief source of the metal. There is little doubt however that the zinc

\* "Nature," Feb. 10, 1916.

TABLE I.  
*Production of Spelter (in metric tons).*

Countries.	1904.	1905.	1906.	1907.	1908.	1909.	1910.	1911.	1912.	1913.
Germany .....	191,060	197,184	205,023	208,707	216,876	220,080	227,747	250,393	271,064	283,113
Belgium .....	139,982	146,592	152,461	154,492	165,019	167,100	172,578	195,092	200,198	197,703
Holland .....	13,069	13,787	14,650	14,990	17,257	18,548	20,975	22,733	23,932	24,323
Great Britain .....	46,216	50,927	52,587	55,595	64,473	68,550	63,078	66,956	57,231	59,146
France and Spain .....	49,082	50,369	53,786	55,733	55,513	61,118	59,141	64,221	72,161	71,023
Austria and Italy .....	9,248	9,357	10,780	11,359	12,781	12,638	13,305	16,876	19,604	21,707
Russia .....	10,606	7,642	9,610	9,738	8,839	7,945	8,631	9,936	8,783	7,610
Norway .....	..	..	..	..	..	..	..	6,680	8,128	9,287
Production in Europe .....	450,293	474,800	498,897	510,614	531,044	542,779	565,455	632,887	661,081	673,912
"    "    United States .....	165,850	183,245	202,092	228,838	189,941	240,446	250,627	267,472	314,512	320,283
"    "    Australia .....	290	650	996	996	1,087	..	508	1,727	2,296	3,724
Total .... about	625,400	658,700	702,000	738,400	722,100	783,200	816,600	902,100	977,900	997,900
Yearly average price .... £	22 11 10	25 7 7	27 1 5	23 16 9	20 3 6	22 3 0	23 0 0	25 3 2	26 3 4	22 14 3

TABLE II.  
*Consumption of Spelter (in metric tons).*

Countries.	1904.	1905.	1906.	1907.	1908.	1909.	1910.	1911.	1912.	1913.
United States .....	157,100	179,000	200,000	227,900	188,300	216,900	214,500	251,600	312,900	313,300
Germany .....	151,800	162,700	179,300	174,400	180,200	188,100	184,500	219,300	225,800	232,000
Great Britain .....	129,100	136,000	140,500	140,700	138,500	155,500	177,800	175,700	185,200	194,600
France .....	67,200	59,700	63,400	69,600	77,900	66,000	56,300	82,000	82,000	81,000
Belgium .....	52,000	49,100	51,000	55,000	68,000	64,600	76,500	73,700	77,200	76,400
Austria-Hungary .....	25,300	26,200	28,300	30,300	32,600	32,800	33,800	43,500	46,800	49,400
Russia .....	23,500	26,000	17,000	17,600	17,800	18,400	24,900	28,900	27,000	33,300
Italy .....	5,100	5,600	6,200	7,100	8,400	8,200	8,100	10,100	10,700	10,800
Spain .....	4,000	4,700	4,700	4,800	5,000	4,500	4,200	4,800	4,700	5,900
Netherlands (estimated) .....	3,700	3,800	3,800	3,800	3,800	4,000	4,000	4,000	4,000	4,000
Other countries (estimated) .....	10,700	11,000	11,000	12,000	10,000	9,000	12,400	17,800	19,700	20,000
Total .....	629,800	663,800	705,200	743,200	730,500	798,900	827,000	911,400	996,900	1,012,700

of the future will be derived largely from concentrates obtained from low grade and complex ores, by gravity, magnetic, flotation, etc., methods of separation. At the present time the chief sources of the world's supply of zinc ores, including concentrates, are the United States, Australia, Germany, Italy, Spain, Algeria, and Tunis. Zinc ores also occur abundantly in China, and increasing quantities are exported by Japan. The total output of dressed zinc ore for the United Kingdom (chiefly Cumberland and Northumberland) is about 17,500 long tons per annum. In 1913, 11,260 tons was exported to Belgium and 1960 tons to France. In the same year the total imports of zinc ore by British smelters amounted to approximately 65,000 long tons, derived mainly from Australia, Italy, Algeria, Germany, Spain, and France. The most important sources of zinc ore in the British Empire are the deposits at Broken Hill. Owing to the shortage of the supply of domestic ores, European smelters have imported for some years considerable quantities of zinc ore from Sardinia, Algeria, Australia, and, in recent years, in increasing amount, from America. The ore is shipped in bulk to Antwerp and Swansea, generally in the calcined or roasted state. The ores are bought on different formulas, of which the following is a type:— $V = 0.0095 P (T - 8) - R$ , where  $V$  is the value in £ per ton,  $P$  the price of spelter (good ordinary brands) in London,  $T$  the percentage of zinc in the ore,  $R$  the returning charge (i.e. cost of smelting per ton), but the value is affected adversely by the presence of impurities, such as lead (which should not exceed 3%), iron and manganese (which should not exceed 10%), and thio-spar.

The following approximate figures, making a total of nearly 900,000 tons, of the European zinc

ore trade in 1913 are available: Zinc ore imported into: Germany 308,000, Austro-Hungary 50,000, Belgium 300,000, France 173,000, England 65,000 long tons.

*Metallurgy of zinc.* Practically all the zinc of commerce is produced by distillation of the oxide with carbon. Calamine ores are calcined in simple shaft furnaces or in reverberatory furnaces. Crushed zinc blende is best roasted in mechanically raked furnaces such as the Zellweger and Merton furnaces, and in muffle furnaces, such as the Hegeler furnace (when the blende is burnt for sulphuric acid manufacture), though double-hearth hand-raked reverberatory furnaces are still in use in Europe. The retorts are best made by hydraulic machines, but hand-made retorts are still largely used. American clays are inferior to European, and do not allow of such high temperatures being employed. Progress in the metallurgy of zinc in recent years has been confined mainly to changes directed towards higher extraction results and the reduction of labour. Thus all modern furnaces are gas-fired, and are mostly worked on the regenerative system.

In direct-fired furnaces the coal consumption is about 2 tons or more per ton of ore smelted, while in modern gas-fired Belgian furnaces the consumption of coal for fuel is about 1.0 ton per ton of ore smelted. For Rhenish gas-fired furnaces the average is about 1.1 to 1.2 ton. With a view to the reduction of the cost of labour, mechanical appliances for charging and cleaning the retorts have been introduced in several European works, and more recently in American works, but they have not met with general favour. The ore charged into the retorts generally contains about 45 to 50% of zinc. The weight of the charge varies with the size of the retorts, the Belgian



retorts in the United States taking about 60 lb., plus a small quantity of by-products, exclusive of reduction material, while for Rhenish retorts in Europe it is from 75 to 90 lb. The plant at Port Pirie, Australia, comprises 10 gas-fired furnaces, each containing 2 tiers of Rhenish retorts back to back, with three rows of 24 retorts in each tier, i.e., a total of 1440 retorts. The charge consists of 10,000 lb. of washed concentrate, 3000 lb. of coke, and 1500 lb. of coal, and the retorts are heated slowly to 1325°—1350° C. With ordinary ores the residue left contains as a rule from 4 to 8% Zn, and a good deal of unburnt coal. This, after screening, and mixing with about 20% of fresh coal, is in some works used as a fuel for boilers. With leady ores, practically all the lead and silver remain in the residues. In such cases these are ground and concentrated and sold to lead smelters. The amount of lead admissible in the distillation process is usually considered to be limited to about 10%, but with care, and the selection of suitable retort materials, it is possible to treat successfully ores containing from 14 to even 20% Pb. In modern German and Belgian practice a 90% yield of spelter is constantly reached with roasted blende carrying 50% Zn; in the Western States of America the yield from a 40% ore is stated to be about 75 to 80%; the yield in this country is usually about 85%. Complex zinc-bearing ores are concentrated by mechanical dressing, electrostatic, magnetic, and flotation processes. The last-named process produces slimes, the metallurgical treatment of which is the greatest problem of zinc smelters at the present time. The loss of zinc in roasting is particularly large, and, in smelting, lead tends to distil over with the zinc. This lead may however be kept back by passing the zinc vapours through charcoal or burnt fireclay filters. When slimes and fine ore are briquetted with bituminous coal and pitch, the filtration which takes place through the pores of the briquettes causes the lead to remain in the carbonaceous residue, this then being suitable for lead smelting. Briquetting has the further advantages of allowing larger charges to be worked, and making the charging and discharging operations more rapid and cleanly. Another successful method of dealing with complex ores is to reduce them in reverberatory furnaces, or in a current of air, whereby the zinc is again immediately oxidised by the carbon dioxide formed, and by the air. The gaseous products carrying the zinc oxide are passed through a cooling tower to a series of woollen bags wherein the oxide is retained. Complex ores are also smelted in electric furnaces, and this process may possibly be advantageously substituted for the retort process where fuel is dear and hydro-electric power easily available. The reduction of carbon dioxide is more incomplete however than in retorts, with the result that a larger amount of fume (blue powder) containing 8 to 10% of zinc oxide, is formed. In the Côte and Pierson process blende is smelted without preliminary treatment. The furnace is circular, with sides and bottom lined with graphite, the top being a low dome of fire-brick. A carbon electrode, which can be raised or lowered, passes through an opening in the centre of the top, whilst the other electrode, a cone of graphite, projects from the hearth. The charge consisting of a mixture of blende, iron, and lime is introduced through the roof into the hot furnace, and the first reaction of iron on lead sulphide is effected at a relatively low temperature. The resulting lead is tapped. The temperature is then raised to induce decomposition of the zinc sulphide by the iron. The zinc distils over, and is condensed in the condenser, the carbon in which is kept at a red heat, to diminish, as far as possible, the formation of zinc fume. Finally, iron sulphide and the slag are run out. Electric

zinc smelting has now passed the mere experimental stage and become a commercial process, but investigations are still proceeding. Complex ores are also successfully treated for the production of chloride or sulphate, with subsequent leaching. The sulphate may be used for the manufacture of lithopone, or treated electrolytically for the production of the metal. The chloride is treated electrolytically and the chlorine utilised for the manufacture of bleaching powder. *Industrial applications of zinc.* The galvanised iron industry probably accounts for about 60% of the world's consumption of spelter, while the manufacture of brass probably utilises another 20 or even 25%, the remainder being used for conversion into sheets and for minor uses. Hot galvanising is now being largely replaced by sheardising and by electrolytic deposition. Zinc exhibits its greatest degree of ductility and malleability between 100° C. and 150° C., between which temperatures it is rolled into sheets. In the manufacture of rolled zinc the usual practice is to cast the metal into thin plates, nor ingots, which while still hot are rapidly passed through the rolls until the desired thickness is attained. Lead is stated not to interfere with the rolling qualities when below 1.25%, but any increase above this is injurious. Cadmium is injurious if above 0.25%, whilst arsenic and antimony are harmful from 0.02% upwards, arsenic in particular having a hardening effect. As little as 0.01% Sn has a bad effect. Copper below 0.08% has no effect, nor iron below 0.12%. Zinc intended for the manufacture of brass which has to undergo severe mechanical treatment, as in the manufacture of cartridge cases, should be of good grade and contain not more than 0.1% Pb and 0.05% Fe. The highest grades of zinc are generally prepared by the employment of pure ores, and by redistillation of ordinary spelter, but some are prepared by electrolysis.

The following analyses of brands of virgin spelter may be taken as typical:—

Brand.	Lead. per cent.	Iron. per cent.	Cadmium. per cent.	Tin. per cent.
Upper Bank (English) ....	2.55	0.15	0.09	0.05
V.M.C. (Belgium)	0.66	0.26	nil	0.03
Vicille Montagne (Belgium) ....	2.00	0.04	0.07	nil
Freiberg (Saxony)	1.03	0.04	0.02	0.07
Lazyshtte (Upper Silesia) .....	1.12	0.02	0.017	nil
Lipine electrolytic (Upper Silesia)	0.06	0.01	0.005	0.02

The impurities are often removed by liquating the metal in large reverberatory furnaces, with sloping hearth, holding from 20 to 30 tons of metal. Amongst the newer zinc alloys are those of aluminium-zinc containing 10 to 20% Zn, with the addition of a little copper, these alloys being largely used for light castings in the automobile industry. *Future of the zinc industry.* Owing to the shortage of spelter brought about by the war, the selling price of the metal has appreciated in England to more than five times its pre-war figure. Very great efforts are being made in the United States to take advantage of the present conditions, and the total capacity of the American plants in process of erection, and completed, will be brought to about 650,000 tons per annum, or just double the output of 1913. The ore reserves in America are large and will no doubt keep the smelting works satisfactorily supplied with ore. In Germany the supply of ore from Silesia, Hungary, Carinthia, and Tyrol will probably be insufficient, but although the importation of ore from Australia is stopped, large quantities of concentrates have

been obtained from China, and this source will no doubt be developed. For some time the total output of Germany and Belgium will probably be only sufficient to satisfy home consumption. Although there will be American competition to contend with, the present would appear to be a very favourable opportunity to expand the spelter industry, of this country, and steps are being

taken to erect new smelting plants both in this country and in Australia. Special inducements are being held out to English smelters, and a scheme has been drawn up, and is under consideration, providing not only for preferential treatment of the Empire's zinc ores, but also allotting a fair share of the raw material to France and Belgium.—T. St.

## Journal and Patent Literature.

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*English.*—6d. each, to the Comptroller of the Patent Office, Southampton Buildings, Chancery Lane, London, W.C.

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### I.—GENERAL; PLANT; MACHINERY.

#### PATENTS.

*Grinding machine or apparatus [for oil-cake, etc.].*  
G. R. Schueler, Hull. Eng. Pat. 12,015, Aug. 20, 1915.

Is a grinding machine suitable for oilcake, a vertical cylinder is provided with a series of blades projecting inwards to an adjustable distance, while a concentric rotating shaft is provided with a series of lateral holes arranged spirally, in which blades similarly adjustable are fixed. The material is fed in at the top and withdrawn at the bottom through lateral openings which are controlled by moving covering plates towards or away from them.—W. F. F.

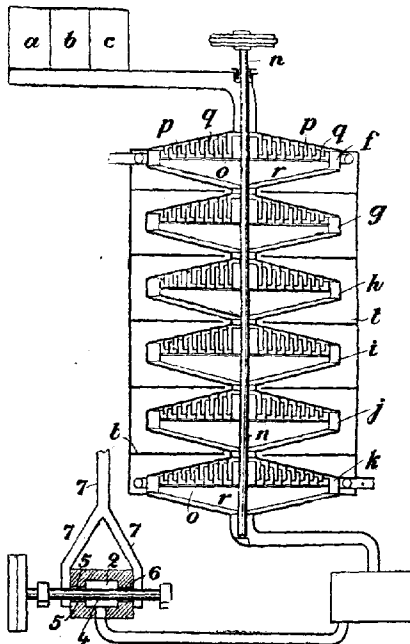
*Grinding-mill.* J. W. Cover, Tacoma, Wash.  
U.S. Pat. 1,194,717, Aug. 15, 1916. Date of appl., Nov. 16, 1915.

A CYLINDRICAL framework is mounted to rotate on a horizontal axis and contains a series of cylindrical pockets just within the outer surface and supported by the end plates, each pocket containing a number of grinding bars which roll upon one another as the frame rotates. The drum rotates with its lower part in a receptacle containing the material to be ground, and the material is taken up by scoops on the drum formed by short circumferential and radial plates, one scoop being provided for each pocket and arranged so as to deliver the material into the grinding pockets as they rise. The circumferential openings between the scoops are provided with screens. The material delivered from the grinding pockets falls on to short radial plates and thence on to a screen in the centre of the apparatus. The screened material is delivered to a shoot extending through an axial opening.—W. F. F.

*Mixing and homogenizing apparatus.* J. Gry, Odder, Denmark. Eng. Pat. 100,077, Feb. 14, 1916. Under Int. Conv., Nov. 25, 1915. (Appl. No. 2193 of 1916.)

The constituents of the mixture are supplied in adjustable proportions by separate pumps, *a, b, c*, to a series of flat, superposed, circular compartments, *f, g, h, i, j, k*. Each compartment contains a horizontal disc, *o*, having projecting teeth, *p*, on its upper surface and spiral guides, *r*, on its lower surface. All the discs are mounted on a vertical rotating shaft, *n*, the teeth, *p*, moving between obliquely inclined teeth, *q*, depending from the top of the compartment. The mixture thus passes into each compartment at the centre, outwards through the moving teeth, and then inwards

between the spiral guides to the next compartment. A cooling medium passes upwards through the casing and is guided by baffles, *t*. The mixture



passes to the homogenizing chamber, 2, provided with outlets, 5, 6, which are adjustable by an axial movement of the slightly conical rotating shaft, 4. The homogenized mixture is delivered to the outlet, 7.—W. F. F.

*Kiln; Continuous.*—F. D. Shaw, Chicago, Ill., Assignor to Shaw Kiln Co., Atlanta, Ga.  
U.S. Pat. 1,194,556, Aug. 15, 1916. Date of appl., Dec. 10, 1910.

The kiln comprises a central chamber having a combustion chamber on each side, and a common arched roof enclosing a space which extends over the combustion chambers and communicates with the central chamber. A moving carriage may be

carried horizontally through a preheating chamber and above the central chamber close to the common roof.—W. F. F.

*Filter.* C. D. Burchenal, New York. U.S. Pat. 1,194,949, Aug. 15, 1916. Date of appl., Mar. 10, 1916.

A FILTER comprises parallel plates with ribs on both faces forming cells, with filtering media between them. A supply passage opens into all the cells, and valve-controlled outlet passages communicate with both faces of each plate.—W. F. F.

*Filter.* R. L. y Guijarro, Habana, Cuba. U.S. Pat. 1,195,000, Aug. 15, 1916. Date of appl., Nov. 5, 1915.

A ROTATING filtering drum is mounted horizontally in a tank the lower part of which is concentric with the drum. The interior of the drum communicates with the hollow perforated central shaft, and a vacuum is maintained within it. Radial vanes are provided to direct the filtered liquid to the central shaft. A conveyor having scraping members partly surrounds the drum and conveys solid material along an inclined trough to a discharge shoot. A baffle plate is provided having one edge in contact with the drum to prevent rotation of the liquid to be filtered.—W. F. F.

*Drying-kiln.* C. Harley, Ludington, Mich., Assignor to L. G. Merritt, Lockport, N.Y. U.S. Pat. 1,194,734, Aug. 15, 1916. Date of appl., Aug. 28, 1915.

A NUMBER of superposed horizontal platens are formed of parallel pipes connected so as to form a continuous coil through which a heating medium is circulated. The platens are connected alternately to two frames one of which is movable. The movable frame is counterbalanced and is raised and lowered alternately so as to bring the platens connected therewith into contact with the upper and lower surfaces of the fixed platens.—W. F. F.

*Sizing or classifying comminuted material; Process of and apparatus for* — H. M. Sutton, and W. L. and E. G. Steele, Dallas, Tex. U.S. Pats. 1,196,047 and 1,196,048, Aug. 29, 1916. Dates of appl., Feb. 5, 1914, and Oct. 8, 1915.

THE material is transported at progressively varying speed over a series of surfaces arranged in steps and inclined to the direction of movement of the material. A progressively varying undulating vibratory motion is imparted to the surfaces, so that the material spreads out transversely to the direction of movement into graduated sizes of grains which are separately collected from the last surface.—W. F. F.

*Carboys for carrying acid or other products; Manufacture of crates or baskets for* — L. Struys, Charleroi, Belgium. Eng. Pat. 101,249, Mar. 28, 1916. (Appl. No. 4551 of 1916.)

*Annealing kiln or oven.* T. W. Ridley, Middlesbrough. U.S. Pat. 1,196,152, Aug. 29, 1916. Date of appl., Feb. 21, 1916.

*Furnaces; Tilting* — H. J. Kitchen, and T. Balmforth and Co., Ltd., Luton. Eng. Pat. 101,310, Mar. 10, 1916. (Appl. No. 3598 of 1916.)

*Fabric for filter-plates and other purposes.* E. J. Sweetland. Fr. Pat. 478,663, May 11, 1915.

SEE Eng. Pat. 7469 of 1915; this J., 1916, 720.

*Filtration, aeration, and gasification of liquids; Apparatus for* — T. K. Irwin. Fr. Pat. 479,670, Sept. 4, 1915.

SEE Eng. Pat. 19,901 of 1914; this J., 1915, 885.

*Separating liquids and solids; Apparatus for* —

J. V. N. Dorr. Fr. Pat. 478,702, May 17, 1915.

SEE U.S. Pat. 1,140,131 of 1915; this J., 1915, 703.

*Tube mill.* J. S. Fasting. Fr. Pat. 478,746, May 19, 1915.

SEE Eng. Pat. 7160 of 1915; this J., 1916, 294.

*Furnaces; Reverberatory* — Manchester Furnaces, Ltd., W. A. Russell, and J. Lord. Fr. Pat. 478,909, June 4, 1915.

SEE Eng. Pat. 6050 of 1915; this J., 1915, 894.

*Desiccating substances containing water.* C. A. R. Steenstrup. Fr. Pat. 479,518, Aug. 14, 1915.

SEE Eng. Pat. 12,046 of 1915; this J., 1916, 521.

## IIA.—FUEL; GAS; MINERAL OILS AND WAXES.

### *Fuel economy. Report of British Association Committee.*

THE Committee points out the wastefulness in regard to our methods of getting and utilising coal, great economies in these directions being attainable. The Committee emphasises the value of the by-products, pointing out the field for greater expansion in the home demands for ammonium sulphate, and for motor spirit manufactured from our coal. Whilst Germany years ago abandoned the use of beehive coke ovens, we still carbonise about 64 million tons in this wasteful type of oven. Attention is drawn to the steady increase in the total output of mines and to the phenomenal growth of the export trade. The importance of organising means to raise the coal left behind in the mines is also mentioned. Owing to the magnitude of the work the General Committee resolved itself into five Sub-Committees. The first Sub-Committee (Chemical and Statistical) is preparing a memorandum and bibliography on the chemistry of coal. Some of the members have undertaken experimental work on the constituents of coal, their mutual relations, and their influence upon the character of the products obtained by distillation or oxidation. The members are of the opinion that the time is ripe for the organisation of a scheme of systematic co-operative research aided by national funds. This section is also considering the purposes for which coal is used and the wastage due to coal left behind in the pits. The second section (Carbonisation) estimates that the amounts of coal used for the manufacture of town gas and metallurgical coke in 1913 were 18,200,000 and 20,000,000 tons respectively. The ammonium sulphate produced was 182,180 tons and 133,816 tons respectively, whilst of the 29 million tons of coal used in coke manufacture 13.3 million tons was carbonised in by-product ovens. This section is endeavouring to secure a complete return of the number of by-product ovens, the character of each installation, coking capacity, type of recovery plant used, number of benzol plants, method of utilising waste heat and surplus gas, etc., in order to arrive at an estimate of the margins of possible economies in coking practice. The section has instituted inquiries as to the present practice in the manufacture of town gas, and later on intends to consider the question of low temperature carbonisation.

The third section (Metallurgical, Ceramic, and Refractory Materials) has taken steps to secure data as to the amount of fuel used in the manufacture of various brands of pig-iron and is preparing a memorandum dealing with the heat balance of a modern blast furnace. The section will deal with the best methods of utilising surplus

gas and the application of dry air to blast-furnaces. Inquiries are being instituted relative to fuel consumption in steel works, and to modern practice in iron foundries, wrought iron and specialised steel industries.

The fourth Sub-Committee (Power and Steam Raising) is to consider the amount of fuel used and the power developed in factories, mines, railways, ships, etc. It will deal with the present position of central electrical power plants and gas undertakings, and will discuss the merits of steam, gas, oil, and petrol engines as power producers. It will investigate the possible saving of fuel under varying conditions and will deal with the use of large turbine and gas-engines, and other aspects of the power question. The last section (Domestic Fuel) estimates that nearly one-fifth of the coal consumption is utilised for domestic purposes. Any reform in domestic fuel consumption should aim at reduction in cost of heating, diminishing the smoke nuisance, and better hygienic conditions in living apartments. The section is arranging for experiments on these lines and is carrying out experimental work on the relative efficiencies of coal-fires, gas-fires, electric heaters, and the like. It is also considering improvements in the construction and installation of open fire grates and the prospects of substituting for raw coal some form of carbonised fuel (semi-coke or coke).—J. E. C.

*Coal; The structure of*—M. C. Stopes and R. V. Wheeler. Brit. Assoc., Section B.—Newcastle, 1916.

SUITABLY prepared transparent sections of coals reveal under the microscope the fact that different parts of the coal substance are composed of different materials. The authors have undertaken the further separation and examination of the different parts of the coal substance, aiming at an ultimate correlation of definite morphological tissues or portions of tissues of the original plants with specific chemical substances now in or yielded by coal. When various coals are treated in a suitable manner, certain vegetable debris, such as wood, spores, and cuticles, can be separated, and from some varieties of coal sufficient of each (botanically) distinct material can be obtained to enable a thorough chemical examination to be made. For example, the authors have obtained a supply of pure cuticle, freed from all other debris of the coal substance, sufficient to allow of a study of its behaviour under different modes of heat-treatment, from which the products of its destructive distillation can be determined and its chemical constitution deduced.

*Coal; Influence of iron pyrites on the oxidation of*—T. J. Drakeley. Chem. Soc. Trans., 1916, 109, 723—733.

EXPERIMENTS are described showing that iron pyrites has a minor effect on the oxidation of coals, and its presence cannot be ignored, even though non-pyritic coals may be amongst those most liable to ignition. A difficulty is experienced in drawing conclusions from the percentage of sulphur in a coal, as pyrites disseminated throughout a coal in microscopical particles will act more effectively than larger quantities of nodular pyrites. Even though samples be drawn from the same seam, it is almost impossible to make inferences from analyses, as great differences may exist in the physical conditions of occurrence. A fault, or a poor roof, may have, it is stated, a more predominating influence than the percentage of sulphur on the ignition of the coal.—B. N.

*Coal; Yield of extract from*—on treatment with benzene. F. Fischer and W. Gluud. Ber., 1916, 49, 1460—1468.

THE yield of extract from coal is greatly increased

by making the extraction at a temperature (about 275° C.) and pressure (about 55 atm.) approximating the critical constants of benzene (288° C., 50 atmos.). Under these conditions ordinary coal yielded 6½% extract, as compared with 0.1 to 0.15% at 80° C.; lignite 25% as against 11%; and cannel coal 4% as against about 1%. Apparently no material decomposition takes place and the original substances of the coal are extracted unaltered.—C. A. M.

*Coal; Extraction of*—by means of liquid sulphur dioxide. F. Fischer and W. Gluud. Ber., 1916, 49, 1469—1474.

ON treating coal with liquid sulphur dioxide it swells up, disintegrates into fine particles, and yields a reddish extract, which on evaporation of the solvent leaves a heavy mobile oil. When this is treated with sodium bicarbonate solution and distilled in a current of steam, it yields a light oil with faint fluorescence and an odour of petroleum. By extracting the residue with petroleum spirit, yellow oils stable in the air and distilling at 200° to 350° C. are obtained. In comparison with benzene extracts made at 275° C. (see preceding abstract), the extracts obtained by means of liquid sulphur dioxide contain much less solid substances. This is also the case with the extracts from lignite. When treated with benzene, lignite yields the so-called montan wax, which is a mixture of a wax with resins, whereas the extract obtained from lignite by means of liquid sulphur dioxide is a typical resin.—C. A. M.

*Coal; Conversion of*—into soluble substances by means of ozone. F. Fischer. Ber., 1916, 49, 1472—1474.

By treatment with ozone the chief constituent of coal, corresponding to the original cellulose, is gradually converted into soluble products. For example, by six successive ozonisations of 14 to 40 hours, 92% of a sample of coal was rendered soluble in water. The soluble substance was dark brown, and had an odour of caramel and a pronounced acid taste. It was slightly soluble in alcohol, very sparingly soluble in ether, and nearly insoluble in petroleum spirit. It dissolved in ammonia, alkali solutions, and acids, and formed precipitates with the acetates of heavy and alkaline-earth metals.—C. A. M.

*Gas from hard wood and heavy oil.* A. M. Hunter. J. Gas Lighting, 1916, 135, 555.

THE Bahia Blanca Gas Company, owing to the recent prohibition of coal exports from England, and to excessive freight charges, have found it impracticable to continue making gas from coal. A process has been evolved in which hard wood is distilled in the ordinary  $\Omega$ -retorts, maintained at a high temperature, and after the first hour, when the wood is incandescent, crude heavy oil, of an asphaltic character, is introduced at a pressure of 80 lb. per sq. inch, through special atomising injectors. The resultant gas may average up to 575 B.Th.U. per cub. ft. and the yield from 8 tons of hard wood and 1.2 tons of heavy oil is approximately 137,700 cub. ft. The gas appears to be permanent and the wood-gas is found capable of carrying the richer hydrocarbon gases from the oil.—J. E. C.

*Sulphate of ammonia; Direct process for the manufacture of*—, and the storage of ammoniacal liquor. W. S. Curphey. Fifty-second annual report (1915) on alkali, etc. works by the Chief Inspector.

THE report notes a further extension in the use of direct methods for the production of ammonium sulphate in coke-oven works and gas-works. THE

influence of these methods on the action of purifiers has been prejudicial to the yield of ammonium sulphate, yields of 12½, 16½, 17, 18, 18½, 19½, 20, 24½, 28 lb. per ton of coal being quoted. The character of the reactions taking place in purifying systems is discussed at length, as well as the effect of temperature, and of certain impurities in the crude gas. The following conclusions are drawn as to the conditions best suited for maintaining the highest efficiency in purifiers: 1. Due hydration of the oxide (5 to 10% moisture). 2. Crude gases should be dry and cool rather than moist and warm. The temperature of the oxide in the sulphiding zone should be about 70° F. (21° C.). 3. The gas should be freed from tar, fog, oils, naphthalene, and hydrocyanic acid; should contain, say, 0.5 to 1 grain of ammonia per 100 cu. ft., and oxygen equivalent to half the volume of hydrogen sulphide present. 4. Purifier boxes should be sheltered and worked so as to bring the material richest in ferric hydroxide into contact with gas richest in hydrogen sulphide. 5. Direction of flow should be downwards. 6. Conditions of working should be regular. Temperature of oxide, and of inlet and outlet gases should be recorded as well as the oxygen content of the gas. Results of observations and tests at several plants are given in full detail. It is suggested that avoidable losses occur at many of the works using the direct process, and it is recommended that care be taken to ensure that the purifier temperature is not lowered by undue exposure of the boxes, that the moisture content is carefully regulated, and that the gas enters the purifiers, cool and dry, with a moderate regulated amount of ammonia. The use of a washer, fed with virgin liquor, and placed between the acid bubbler and the purifiers, has much to recommend it. Low working temperature of the purifiers might be corrected by introducing a steam pipe.

Attention is again drawn to the seriousness of the loss sustained by ammoniacal liquor when stored in contact with air, and the marked advantages of covering the liquor with a layer of mineral oil are clearly shown in tables giving actual results at various works (see this J., 1915, 1247). It is suggested that all pipes conveying liquor should be lengthened so as to seal the ends, and thus avoid a fall through the air of the entering liquor.

—J. E. C.

*Corrosion in a steel gasholder tank.* W. Wilson. North British Assoc. of Gas Managers. Sept. 1, 1916. *J. Gas Lighting*, 1916, 135, 504—506.

ANALYSIS of the tank water showed the presence of ammonium carbonate and compounds of ammonia with weak organic acids. At least two grains per gallon of a liquid fatty acid was present, similar to that contained in linseed oil, and apparently the acids were not derived from tar. The author concluded that ammonia had slowly acted on the linseed oil of the paint or on the free fatty acids therein, forming an ammonium soap, alkaline to litmus, decomposing on boiling and leaving acid behind. This might account for the destruction of the paint but not for the corrosion of the metal. On emptying the tank considerable incrustation was found. The deposits were brown or blue, and generally blue next to the plates which were badly corroded. A further analysis of the tank water showed iron in solution, produced by corrosion of the metal by organic acids. Various theories as to the cause of the corrosion are discussed. The tank sides had since been thoroughly scraped and brushed with steel wire brushes, and painted with "Bituferri" enamel. The bottom had been cleaned, dried, and then covered with a ½ inch layer of plastic pitch. The tank was to be filled with pure water and a

film of oil placed on the surface to prevent absorption of cyanogen compounds from the gas.

—J. E. C.

*Sulphur in coal gas; Rapid method for the determination of —.* F. Mylius and C. Hüttner. *Ber.*, 1916, 49, 1428—1443.

THE combustion method for the determination of sulphur in coal gas has been modified to give a more rapid method. A quartz combustion tube, 30 cm. long, contains a tightly wound roll of the finest platinum gauze, 15 cm. long, to which is attached a small spiral of the finest platinum wire, which serves to ignite the gaseous mixture; the gas-air mixture is burnt completely in the first portion of the roll, which is heated to 300°—400° C., the sulphur dioxide is converted into trioxide in the intermediate portion at a lower temperature, and the trioxide and steam are condensed to sulphuric acid in the cooler portion of the catalyst. The sulphuric acid produced is later rinsed out from the quartz tube and titrated with N/1000 sodium carbonate solution, using as indicator an ethereal solution of iodoosin (Mylius and Foerster, this J., 1891, 856). The removal of carburetting agents from Berlin illuminating gas has led to a decrease in the sulphur content. Phenylhydrazine may be used for the removal of sulphur on a small scale. Porous platinum, i.e., a roll of finest platinum gauze, is suitable for the absorption of small amounts of sulphuric acid from acid gases.

—F. W. A.

*Hydrogen; Volumetric determination of — by oxidation with activated chlorate solution. Removal of carbon monoxide by means of mercuric chromate.* K. A. Hofmann. *Ber.*, 1916, 49, 1650—1662.

THE oxidation of hydrogen by means of activated chlorate solutions at ordinary temperatures in Hempel absorption pipettes presents certain advantages over the method of combustion by means of palladium-asbestos. The pipette is prepared by filling it as completely as possible with platinised porous tubes or rods, allowing 5 c.c. of 1% palladium chloride solution to flow on to the ends of the rods nearest the capillary where it is dried off by means of a small flame, and finally running in a solution of 5 grms. of sodium bicarbonate, 35 grms. of sodium chlorate, and 0.01 gm. of osmium dioxide in 250 to 300 c.c. of water. The full activity of the solution is not exhibited till 200—300 c.c. of hydrogen has been absorbed, but it is then capable of oxidising at least 60—70 c.c. in ten minutes, and this velocity is maintained for more than 100 determinations if contact poisons are scrupulously excluded, a condition which is fulfilled if the other constituents in a gaseous mixture are removed in the order usual in gas analysis. The oxidation is not affected by the presence of methane, which, moreover, is itself unattacked. In the case of gases of very high hydrogen content, it is sometimes advisable to dilute with carbon dioxide previous to the hydrogen absorption, as otherwise the oxidation of the last few c.c. of hydrogen may be very slow owing to the platinum-palladium contact material being almost entirely covered by the liquid in the pipette and thus rendered inoperative. The presence of as little as 0.1—0.2 c.c. of carbon monoxide, a quantity which always remains unabsorbed by the ordinary cuprous chloride pipette, causes a very great retardation in the oxidation of the hydrogen. Its complete removal is therefore necessary, and the best method at present found consists in passing the gas, after constant volume has been attained in the cuprous chloride pipette, into a second pipette prepared by introducing 10 c.c. of a paste of freshly precipitated

mercuric oxide on porous tile and charging with a solution of 25 grms. of chromic anhydride in 250—300 c.c. of water. This mixture oxidises 15—20 c.c. of carbon monoxide and 0.9—1 c.c. of hydrogen in 10 mins., and by means of it the last traces of the former gas can be removed.—G. F. M.

*Contact poisons; Retardation by carbon monoxide of the oxidation of hydrogen in the chlorate pipette, a contribution to the knowledge of —.* K. A. Hofmann and H. Schibsted. Ber., 1916, 49, 1663—1669.

The retardation of the oxidation of hydrogen in the chlorate pipette by carbon monoxide (see preceding abstract) is a phenomenon of contact poisoning. Although pure carbon monoxide is itself continuously though slowly oxidised in the pipette, yet as little as 0.2% in hydrogen is sufficient to retard the oxidation of the latter over a long period. The pipette accordingly furnishes an extremely sensitive means of detecting minute traces of this gas. The injurious effect of carbon monoxide does not persist after the removal of the gas if the contact metal is allowed to remain covered for a short time with the osmium-containing chlorate solution. The carbon monoxide does not act as a mechanical poison, i.e., by excluding the hydrogen from the active surface of the contact, since it is itself much more incompletely and slowly absorbed than is the hydrogen, but in some specific chemical way, at present unexplained, it retards the actual oxidation process. Confirmation of this is found in the fact that increase in concentration of the active oxidising agent, e.g., by the addition of oxygen to the gaseous phase, very notably increases the reaction velocity. Both of the oxidation of carbon monoxide alone, and of mixtures of carbon monoxide and hydrogen.

—G. F. M.

*Sodium pyrogallate as a reagent for the determination of oxygen.* J. W. Shipley. J. Amer. Chem. Soc., 1916, 38, 1637—1701.

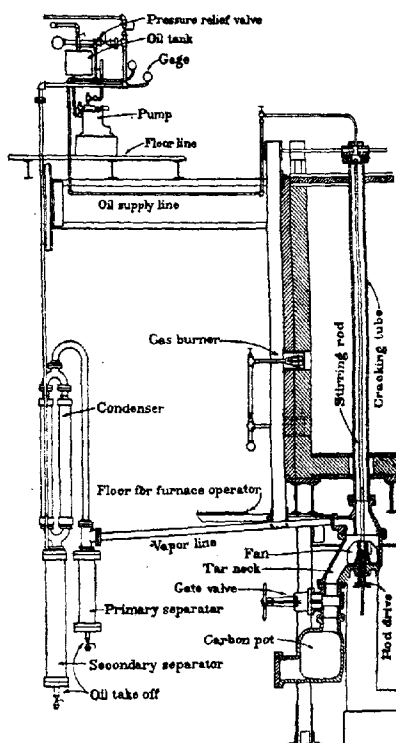
SODIUM pyrogallate solutions of suitable composition have been found to give better results than potassium pyrogallate solutions for the determination of oxygen in gaseous mixtures. The specific absorption (Anderson, this J., 1915, 853) of a solution composed of 7.36 grms. NaOH, 10 grms. pyrogallol, and 11.62 grms. water is five times that of the most efficient potassium pyrogallate solution (Anderson, loc. cit.), and this solution is recommended for use in technical gas analysis. It is somewhat viscous, and when the gas pipettes available have capillaries of less than 1.5 mm. internal bore, it is advisable to use a solution containing 7.36 grms. NaOH, 2—3 grms. pyrogallol, and 8.62 grms. water. No carbon monoxide is formed by the use of these sodium pyrogallate solutions. A new form of double pipette for use with liquid reagents is described.

—A. S.

*Gasoline and benzene-toluene from petroleum and other hydrocarbons; Manufacture of —.* W. F. Rittman, C. B. Dutton, and E. W. Dean. U.S. Bureau of Mines, 1916. Bull. 114. Petrol. Techn. 29, 268 pages. (See also this J., 1914, 626; 1915, 1109; 1916, 525).

The large-scale development of the benzene-toluene and gasoline processes was the result of investigations made jointly by the U.S. Bureau of Mines and the Aetna Explosives Co. of New York. As finally adopted for commercial operation, the benzene-toluene plant consisted of 6 furnaces, each heated by 22 gas-burners and containing 2 rows of 5 vertical cracking tubes (11½ ft. long and 8 in. in diameter), i.e., 60 tubes in all; each tube was provided with a separate oil-feed and condenser, the arrangement being as shown in the

accompanying figure. The removal of deposited carbon from the walls of each tube was effected during operation by means of wiping chains attached spirally to a central rotary stirring rod, this device requiring to be removed and cleaned every few days. The oil was fed at the rate of about 15 galls. per tube per hour in the benzene-toluene process, and at double this rate in the gasoline process; in both processes a much higher rate could be used after preheating the oil. A large number of petroleum oils, ranging in character from crude oils to gas oils and cylinder stocks, were used and, as in the case of laboratory experiments, the reactions desired were found to be practically independent of the kind of oil em-



ployed. The benzene-toluene process was also efficiently operated on other liquid hydrocarbon materials such as solvent naphthas and light oil distillates from water-gas tars and coal tar. Apart from the greater yields obtainable from these materials (2 or 3 times that from ordinary petroleum oils), the use of light oil distillates was found to be advantageous on account of the decreased carbonisation and the lower pressure required for the conversion, the results being as favourable at atmospheric pressure or with a vacuum as with higher pressures. As regards gas formation, 40 to 60 cub. ft. of permanent gas was generated per gallon of oil cracked in the benzene-toluene process; and since only 250 to 300 cub. ft. per tube per hour was required for the furnaces, a large surplus of gas of high calorific value (1000—1400 B.Th.U. per cub. ft.) was available for general plant purposes and other industrial uses. Very small amounts of gas were produced in the gasoline

process, the latter requiring an external supply of gaseous or oil fuel. The gasoline process was tested in the single-tube furnaces employed in the development of the benzene-toluene process, no large commercial plant being available; results distinctly favourable to operation on the large scale were obtained. With single-stage operation (i.e., without re-running the unconverted residuum) the amounts of products recovered in the benzene-toluene process were: benzene, 6–8%; toluene, 6–8%; xylenes, 4–6%; gasoline, 6–8%; creosote oil and pitch (including higher aromatic hydrocarbons and lubricating oil), 25–30%; carbon, 3–5%; and gas, 45–60% of the original oil. In the gasoline process the amount of gasoline recovered was 25–30%, and the residuum (above 150° C.) available for re-running, 70–73% of the original oil. The cost of a unit installation of 4 tubes for the benzene-toluene process, under conditions as in 1915, has been estimated at approximately \$5500 (about £1146) per tube, this sum including the building and all equipment but not the cost of storage tanks or apparatus for the treatment of the furnace products. The cost of a gasoline plant would be considerably less. A comprehensive bibliography, compiled by M. S. Howard, and containing brief abstracts of all the publications mentioned, is appended.—W. E. F. P.

*Aromatic hydrocarbons from a paraffin base oil; The time factor in the formation of —.* G. Egloff and T. J. Twomey. *Met. and Chem. Eng.*, 1916, 15, 245–250.

THE effect of the time factor or rate of oil flow has been studied in connection with the formation of benzene, toluene, and xylene from a paraffin base oil. The oil was cracked at a constant temperature of 700° C., and at 150 lb. pressure, the rates of flow being 12, 16, 23, 30, and 36 galls. per hour respectively. As the time factor increased, i.e., with a diminished rate of oil flow, the percentage of recovered oil decreased from 65.5 to 17.5%, and the sp. gr. of the oil increased from 0.879 to 0.978 at 15.5° C., the effects being similar to those produced by increasing the temperature of cracking. The maximum quantity of benzene in the recovered oil, viz., 26.3%, was obtained at the rate of 12 galls. per hour, the benzene formation increasing with decrease of the rate of oil flow. The maximum percentages of toluene (13.8%) and of xylene (5.9%) were both obtained at the rate of 16 galls. per hour. Toluene and xylene showed an increase, and then a decrease, while benzene increased continuously with increase of the time factor. On the basis of the oil used, the maximum proportion of benzene (6.6%) was obtained at 12 galls. per hour, of toluene (4.1%) at 16 and 23 galls. per hour, and of xylene (2.4%) at 23 galls. per hour. The percentage of recovered oil distilling up to 170° C. increased with increase of the time factor to a maximum of 44.7%, and then decreased, and the sp. gr. of the distillate increased to 0.875. The recovered oil obtained at a rate of 12 galls. per hour, yielded practically pure benzene, toluene, and xylene on fractionation. No regularity was apparent in the distillation fractions above 170° C., with the exception of tar or pitch, the formation of which decreased with increase of the rate of oil flow. Under the conditions of the experiments, a maximum total of 12.5 galls. of benzene, toluene, and xylene was obtained from 100 galls. of oil used at the rate of 16 galls. per hour at 700° C. and a pressure of 150 lb. per sq. in.—B. N.

*Octylene; Action of sulphur on — under pressure.* W. Friedmann. *Ber.*, 1916, 49, 1551–1554.

The following substances were isolated from the product of the action of sulphur on octylene (methyl-*n*-amylethylene) at 270°–280° C. under

pressure: a thiophene derivative,  $C_8H_7S$ , in about 20% yield, identical with that obtained under similar conditions from octane (see this J., 1916, 957); a substance  $C_{10}H_{12}S$ , b.p. 160°–162° C., which is probably a dimethyldiamylthiophene although not giving the indophenin reaction; and a substance  $C_{14}H_{18}S_2$ , which as it is not a disulphide, is probably a dicyclic compound produced by the union of the two first-mentioned substances with elimination of two atoms of hydrogen.—G. F. M.

*Ethane-propane fraction from natural gas condensate; Thermal decomposition of the —.* J. E. Zanetti and E. H. Leslie. *J. Ind. Eng. Chem.*, 1916, 8, 777–779.

THE ethane-propane fraction from natural gas is placed on the market in cylinders under 500–1000 lb. pressure. The gas used in the experiments was free from carbon dioxide and contained less than 0.5% of unsaturated hydrocarbons. As in the case of the propane-butane fraction (this J., 1916, 957), the percentage of unsaturated hydrocarbons in the gaseous decomposition-products increased gradually to a maximum at about 750° C., and then decreased to a minimum at about 950° C. The hydrogen content increased slowly at first with rise of temperature, but a marked increase was shown above 750° C. Formation of aromatic hydrocarbons (tar fog) began at about 750° C. The highest yield of tar fog was 2.5 c.c. per cb. ft. of gas used. The tar contained a large proportion of naphthalene; benzene was also present but no toluene. Copper had no marked effect on the decomposition, but in presence of iron the formation of tar fog was inhibited, and decomposition into carbon and hydrogen promoted.—A. S.

*Deterioration of leather used in gas meters.* Lamb. See page 989.

*Behaviour of chromous salts towards acetylene, and the reducing action of salts of divalent chromium.* Traube and Passarge. See VII.

#### PATENTS.

*Fuel; Manufacture of compressed —.* J. Hani. *Paris. Eng. Pat.* 101,166, Jan. 19, 1916. (Appl. No. 870 of 1916.)

BRIQUETTES are made from a mixture of 95 parts of washed anthracite duff, 3 parts of pitch or bitumen, and 2 parts of disintegrated white spar silica.—J. E. C.

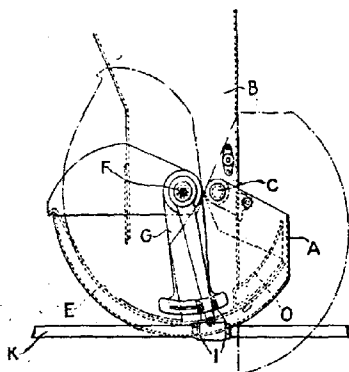
*Gas retorts; Setting of —.* H. A. Carpenter, Sewickley, Pa., and The Riter-Conley Manufacturing Co., Leedsdale, Pa., U.S.A. *Eng. Pat.* 101,117, June 8, 1915. (Appl. No. 4129 of 1916.)

HORIZONTAL retorts are built up of a large number of preformed blocks, preferably of silica material, and are arranged in vertical rows. The retorts are supported by cross supporting walls also built up of preformed blocks. The retorts and supporting walls, as assembled, assume a partially collapsed condition, certain joints being left open to an extent governed by the known rate of expansion of the material. On attaining the working temperature the blocks of the retorts are brought into close contact with each other and with the blocks of the columns. Dowel pins contacting with recesses in the faces of the blocks may be used to prevent displacement of the blocks whilst heating up.—J. E. C.

*Vertical retorts; Discharging apparatus for —.* S. Glover, St. Helens, and J. West, Southport. *Eng. Pat.* 11,942, Aug. 18, 1915.

A TROUGH, a, forming a stationary water-seal, is attached to the mouth, b, of a vertical retort, by means of trunnions, c. Within this trough is

provided a tray-like element, e, carried by the trunnions, f, and adapted to be oscillated by the arms, g, the length of stroke being regulated by



the adjustable stops, i. On moving the tray to the left by means of the rods, k, the raised portion, o, pushes forward a portion of the coke, whilst on the return stroke, a portion of the coke is forced over the delivery edge. To allow access to the retort for scurfing or other purposes, the trough, a, and the tray, e, may be turned to the positions shown in dotted lines.—J. E. C.

**Gas producer plants; Generator for** — G. H. Allen, North Fremantle, W. Australia. Eng. Pat. 10,881, July 27, 1915. Under Int. Conv., July 27, 1914.

AIR is introduced into a continuous gas producer from below the grate by means of an air intake passing through the fire zone to a convenient height. The air then passes downwards through the fuel to a chamber below the grate, whence the gas produced is withdrawn.—J. E. C.

**Gas making apparatus.** A. M. Stanley, Lynn, Mass., Assignor to Hydrocarbon Converter Co., New York. U.S. Pat. 1,177,904, Apr. 4, 1916. Date of appl., Aug. 31, 1910.

THE apparatus consists of a series of cylinders arranged to form concentric passages. The innermost cylinder consists of a porous refractory material of an earthy nature. Immediately outside this is a self-contained heating jacket, the heat being supplied by exhaust gases, etc. Surrounding this heating jacket is another concentric space for heating the air supply to the apparatus. Liquid fuel, along with a regulated supply of heated air from the outermost jacket, passes into the interior of the porous cylinder, its course being checked by baffles. Here, the fuel is gasified by partial combustion. The temperature is regulated by the intermediate heating jacket and a thermostat arrangement operated by the expansion of the vessel.—J. E. C.

**Gas; Process of generating tarless** — H. F. Wallmann, Chicago, Ill., Assignor to A. W. R., and H. H. Wallmann, Chicago, Ill. U.S. Pat. 1,195,934, Aug. 22, 1916. Date of appl., Dec. 17, 1912.

FUEL is passed continuously through a conduit in which it is subjected to distillation, and the solid residue is subjected to a higher temperature in another chamber. Liquid hydrocarbons are led into this second chamber and are gasified, whilst the solid residue is completely consumed in the lower portion by a supply of air.—J. E. C.

**Washer scrubbers for use in the purification of gas.** E. Hanappe, Highgate. Eng. Pat. 101,106, Feb. 17, 1916. (Appl. No. 2392 of 1916.)

THE scrubber is filled with small, regularly shaped sticks or splints of wood placed indiscriminately.—J. E. C.

**Hydrocarbons; Process and apparatus for cracking** — and separating the resulting products. G. F. Lewis, London. Eng. Pat. 7535, May 19, 1915.

LIQUID hydrocarbons are heated under pressure and allowed to escape into a low-pressure chamber. The condensed liquid from the latter is heated in a still and the vapours fractionally condensed. The residue from this still may be returned to the cracking plant or destructively distilled till all volatile matter is driven off, leaving a residue of coke. One or more stills may be used for treating the liquid residues either from the low-pressure chamber or from another still. The stills may be operated at different temperatures and the fixed gases may be led to a suitable gasholder.—J. E. C.

**Petroleum oils; Apparatus for heating** — M. J. Trumble, Artesia, Cal., Assignor to The Simplex Refining Co. U.S. Pat. 1,194,577, Aug. 15, 1916. Date of appl., Sept. 10, 1912.

PETROLEUM oil is passed through a series of tubular retorts and U-connections heated by interior steam jet pipes. A by-pass is arranged to draw gas from the retorts and deliver it into the heated oil outlet pipe.—J. E. C.

**Gasoline from natural gas; Process of extracting** — J. P. Foucart, Muskogee, Okla. U.S. Pat. 1,195,158, Aug. 15, 1916. Date of appl., May 11, 1914.

NATURAL gas is forced into steam which is under a pressure of 20 lb. per sq. in., whereby the constituents which are not in a state of vapour are vaporised. The mixture is then led out of one end of the containing vessel, while a fresh charge of steam and gas is introduced at the other end. The mixture is passed through a condenser and the condensed liquid is collected in a closed tank, in which the gasoline and water form two layers which can be drawn off separately, while the residual gas is withdrawn from above the surface of the liquid.—J. H. J.

**Asphaltic products and process of making the same.** L. Kirschbraun, Chicago, Ill. U.S. Pat. 1,194,750, Aug. 15, 1916. Date of appl., Mar. 29, 1912.

SEMI-ASPHALTIC petroleum residue is heated at a temperature increasing to 700° F. (about 370° C.), and superheated steam, at a temperature not above 700° F., is blown into the mass. A considerable portion of paraffin hydrocarbons is expelled, leaving a highly ductile product.—J. E. C.

**Coke oven doors.** J. E. Mitchell and H. Morfe, Barnsley. Eng. Pat. 13,819, Sept. 29, 1915.

**Gas retorts; Apparatus for charging** — H. Bird, R. Cort and Son, Ltd., and A. G. Sims, Reading. Eng. Pat. 12,776, Sept. 7, 1915.

**Burning gas; Means for** — I. Hall, Birmingham. Eng. Pat. 12,695, Sept. 4, 1915.

**Combustion residues from locomotives; Utilisation of** — J. S. Bean and H. Nash. Fr. Pat. 479,298, July 17, 1915.

SEE Eng. Pat. 14,618 of 1914; this J., 1915, 824.

**Agglutinant for briquettes, etc.** P. J. Mitchell and A. C. Evans. Fr. Pat. 479,635, Sept. 2, 1915.

SEE Eng. Pat. 19,933 of 1914; this J., 1915, 899.



*Fuel; Manufacture of artificial or agglomerated* — H. Faraday. Fr. Pat. 479,640, Sept. 3, 1915.

SEE Eng. Pat. 19,495 of 1914; this J., 1915, 824.

*Coke; Manufacture of — from non-coking or difficultly coking coal.* T. M. Hickman. Fr. Pat. 478,823, May 27, 1915.

SEE Eng. Pat. 4214 of 1914; this J., 1915, 706.

*Coke; Manufacture of —.* A. McD. Duckham. Fr. Pat. 479,372, July 23, 1915.

SEE Eng. Pat. 17,502 of 1914; this J., 1915, 787.

*Retort for distilling or carbonising coal or other carbonaceous substance.* C. W. Tozer. Fr. Pat. 478,040, Mar. 15, 1915.

SEE Eng. Pat. 7116 of 1914; this J., 1914, 912.

*Retorts for carbonisation of coal and the like.* A. McD. Duckham. Fr. Pat. 479,373, July 23, 1915.

SEE Eng. Pat. 13,934 of 1914; this J., 1915, 1044.

*Coal gas making apparatus.* L. D. Carroll, London. From C. S. Chrisman, Philadelphia. U.S.A. Eng. Pat. 101,306, Feb. 24, 1916. (Appl. No. 2783 of 1916.)

SEE U.S. Pat. 1,176,432 of 1916; this J., 1916, 527.

*Shale or coal; Distillation of — for production of oil-gas or lighting gas.* J. W. Fell. Fr. Pat. 478,652, May 10, 1915.

SEE Eng. Pat. 6613 of 1915; this J., 1916, 626.

*Gas producer.* G. H. Bentley and E. G. Appleby. Fr. Pat. 477,998, Mar. 12, 1915.

SEE Eng. Pat. 9040 of 1914; this J., 1915, 540.

*Oil-gas; Manufacture of —.* Hollandsche Residugas Maatschappij Systeem Rincker-Wolter. Fr. Pat. 478,836, Mar. 23, 1915.

SEE Eng. Pat. 6285 of 1915; this J., 1916, 625.

*Gas; Manufacture of —.* Anglo-Mexican Petroleum Products Co., and R. P. Brousson. Fr. Pat. 479,751, Sept. 16, 1915.

SEE Eng. Pat. 6873 of 1915; this J., 1916, 958.

*Carbon monoxide; Method of absorbing — [from gases].* W. Gaus, Assignor to Badische Anilin und Soda Fabr., Ludwigshafen, Germany. U.S. Pat. 1,196,101, Aug. 29, 1916. Date of appl., Oct. 21, 1914.

SEE Ger. Pat. 282,505 of 1913; this J., 1915, 651.

*Hydrocarbons of low boiling point; Production of —.* Iroline Co. of America. Fr. Pat. 477,891, Mar. 5, 1915.

SEE Eng. Pat. 3327 of 1915; this J., 1916, 828.

*Fuel for internal combustion motors.* R. Wood. Fr. Pat. 478,070, Mar. 17, 1915.

SEE Eng. Pat. 24,262 of 1914; this J., 1915, 483.

*Motor compound; Process and apparatus for production of a liquid —.* B. L. Rinehart. Fr. Pat. 478,614, May 5, 1915.

SEE Eng. Pat. 6290 of 1915; this J., 1916, 104.

*Hydrocarbons; Treatment of liquid —.* New Process Oil Co. Fr. Pat. 478,316, Apr. 7, 1915.

SEE Eng. Pat. 4856 of 1915; this J., 1916, 528.

## II.B.—DESTRUCTIVE DISTILLATION; HEATING; LIGHTING.

*A source of floatative agents [for ore concentration].* [Wood tar from saw brush.] Clevenger. See X.

## PATENTS.

*Destructive distillation of coal or other carbonaceous substances; Furnace settings for —.* S. N. Wellington, London. Eng. Pat. 7769, May 25, 1915.

In a furnace setting for vertical retorts, the horizontal heating flues are divided into three spaces by two vertical partitions. Gas and air are fed into the central combustion space, and the heating gases pass to one end, and are then deflected into the two outer spaces adjoining the retorts proper. The proportion allocated to either of the outer spaces is controlled by an angular damper block. The exhaust and air supply flues communicate with a recuperator or regenerator.

—J. E. C.

*Oils, spirits and gases; Method of and apparatus for obtaining — from peat or other material or substances.* A. N. Macnicol, Melbourne, Australia. Eng. Pat. 10,679, July 22, 1915. Under Int. Conv., July 22, 1914.

THE apparatus consists of a retort and a separately heated retort extension. The material is heated in the main retort along with catalytic agents, such as iron oxide, nickel, etc., and in presence of steam, hydrogen, or water-gas. The volatilised oils are then heated in the extension, with or without steam, etc. Condensers are used, and any part of the system may be subjected to pressure by means of a compressor with the necessary valves.—J. E. C.

*Volatile products; Separation of — from solid carbonaceous material.* L. Del Monte y Aldama, Assignor to Oil and Carbon Products, Ltd., London. U.S. Pat. 1,196,470, Aug. 29, 1916. Date of appl., Sept. 21, 1914.

SOLID carbonaceous material is distilled in an inclined retort. The upper end of the retort is heated to a higher temperature than the remainder, and the distilled vapours on their passage to the lower end are condensed by contact with progressively cooler material. The liquid condensed products are prevented from returning to hotter regions of the retort.—J. E. C.

*Charcoal powder; Process of making active —.* J. Pilaski, Warsaw, Russia. U.S. Pat. 1,195,720, Aug. 22, 1916. Date of appl., Aug. 7, 1913.

SEE Ger. Pat. 267,443 of 1912; this J., 1914, 216.

*Neon lighting.* G. Claude. Fr. Pat. 478,076, July 16, 1914.

SEE Eng. Pat. 8312 of 1915; this J., 1915, 1005.

*Metallic filaments for electric incandescence lamps; Manufacture of —.* K. Nishimoto. Fr. Pat. 478,603, May 14, 1915.

SEE Eng. Pat. 7829 of 1915; this J., 1916, 731.

*Heating furnaces [for metals].* Eng. Pat. 15,226. See X.

## III.—TAR AND TAR PRODUCTS.

*Toluene; Formation of — by the action of anhydrous aluminium chloride on xylene and benzene.* F. Fischer and H. Niggemann. Ber., 1916, 49, 1475—1482.

By boiling xylene with 2 to 4% of aluminium chloride for 2 hours beneath a reflux condenser, about 12% of toluene may be obtained, together with a certain proportion of benzene and of higher homologues of xylene. By using the so-called "solvent benzol I" (a mixture of alkylbenzenes yielding 3% distilling up to 134° C.) instead of xylene, only a small amount of toluene is produced, although products of lower boiling point are

formed. In the case of "solvent benzol II" (which yields 2% distilling up to 140°C.) no products of lower boiling point are formed. The energetic action of aluminium chloride causes decomposition of benzene, but only traces of toluene are produced. Attempts to transfer a methyl group from xylene to benzene by the simultaneous decomposing and synthetic action of aluminium chloride gave indecisive results.—C. A. M.

*Chlorination of hydrocarbons with aqua regia.* R. L. Datta and F. V. Fernandes. J. Amer. Chem. Soc., 1916, 38, 1809—1813.

FURTHER experiments have been made on the action of *aqua regia* on aromatic hydrocarbons compare this J., 1914, 1198). *m*-Xylene yielded the monochloro-, the 4,6-dichloro-, and the tetrachloro-derivatives, together with a small quantity of a trichloro-derivative (m.pt. 117°C.). *p*-Xylene yielded the monochloro-, the 4,5-dichloro-, and the tetrachloro-derivatives. *p*-Xylene yielded the monochloro-, the 2,5-dichloro-, and the tetrachloro-derivatives. From ethylbenzene the chief product was monochloroethylbenzene,  $C_8H_7Cl$ ; when the action was prolonged, a crystalline substance of m.pt. 171.5°C., which is under investigation, was formed. Dibenzyl yielded *p*-dichlorodibenzyl. Higher homologues and more complex hydrocarbons gave complex mixtures of reaction products, or were completely decomposed, with formation of chloropiricin.—A. S.

*Chloropiricin and tetrachloroquinone [chloranil]; Formation of — by the action of aqua regia on organic substances.* R. L. Datta and N. R. Chatterjee. J. Amer. Chem. Soc., 1916, 38, 1813—1821.

THE action of *aqua regia* on a large number of organic substances has been studied, and it has been found that in all cases where the compound is destroyed by the action of *aqua regia* chloropiricin is formed, though in very varying quantities (compare this J., 1915, 377). Many aromatic compounds yield chloranil (tetrachloroquinone) by the action of *aqua regia*. This is especially the case with compounds having easily replaceable groups in the *para*-position and compounds of quinonoid structure. Chloranil is not formed from compounds, such as naphthalene and anthracene derivatives, containing complex nuclei. The existing method for the commercial manufacture of chloranil by the oxidation of trichlorophenol with potassium bichromate, could probably be advantageously replaced by a method in which *aqua regia* is used. The following yields of chloranil were obtained by the action of *aqua regia* on 20 grms. of the substances mentioned: quinol, 13—14 grms.; *p*-phenylenediamine, 13—14 grms.; trichlorophenol, 10 grms.; sulphanilic acid, 6—7 grms.—A. S.

2,3-Dihydroxytoluene (isohomocatechol) and the nitro-derivatives of its methyl ethers. R. Majima and Y. Okazaki. Ber., 1916, 49, 1482—1496.

2,3-DIHYDROXYTOLUENE, the lowest homologue of hydrourushiol (this J., 1916, 128), behaves in an analogous manner to the latter on treatment with iron chloride and alkali, and the dimethyl ethers of both substances yield analogous mono- and dinitro-derivatives (see this J., 1914, 91). Amino-2,3-dimethoxytoluene was converted by the diazo reaction into hydroxy-2,3-dimethoxytoluene, which was transformed into the quinone. The hydroxy or amino group appeared to be in the 5-position, whilst comparison with nitro compounds of veratrol indicated that the dinitro derivative is 5,6-dinitro-2,3-dimethoxytoluene. Cain and Simonsen (Trans. Chem. Soc., 1914, 105, 156)

described both nitro derivatives, but the melting points of their products (viz. 76°—77°C. and 95°C.) did not correspond with those found by the authors (viz., 105°—106°C. and 112°—113°C. respectively). The discrepancy is attributed to the preparations of Cain and Simonsen being 4,6-dinitro-2,3-dimethoxytoluene and 4-amino-6-nitro-2,3-dimethoxytoluene. This was confirmed by the preparation of the 4- and 6-mononitro-derivatives from 2-methoxy-3-hydroxytoluene, and the conversion of the 4-nitro derivative into 4-nitro-2,3-dimethoxybenzoic acid, which Cain and Simonsen were unable to obtain. It melted at 94° to 95°C. All the theoretically possible nitro-derivatives of 2,3-dimethoxytoluene have thus been prepared. The 4,5-trinitro derivative melted at 131°—132°C.—C. A. M.

*Phenol ethers, and esters; Hydrolysis of — by means of the hydrochlorides of aromatic bases. Preparation of anilides and their homologues.* A. Klemenc. Ber., 1916, 49, 1371—1376.

ONE molecular proportion of the ether or ester is heated to fusion (180°—230°C.) with 2 to 3 mols. of aniline hydrochloride, or a homologue; the reaction is generally complete within an hour, when the fused mass is poured into concentrated hydrochloric acid and the product worked up by suitable means. With aniline hydrochloride anisic acid gave an 80% yield of *p*-hydroxybenzoic-anilide (m. pt. 201°—202°C.); *m*-methoxybenzoic acid gave *m*-hydroxybenzoic-anilide (m. pt. 156°C.); pyrogalloltrimethyl ether gave pyrogallol (m. pt. 132°C., after one recrystallisation from benzene); 14 grms. of hemipinic acid gave 4 grms. of nor-hemipinic-anil,  $C_{11}H_9O_3N$  (m. pt. 226°C.); anisol is unattacked even after several hours heating in an autoclave. With *p*-toluidine hydrochloride anisic acid gave a quantitative yield of *p*-hydroxybenzoic-*p*-toluidide (m. pt. 207°—209°C.); with *m*-toluidine hydrochloride a high yield of the *m*-toluidide was obtained. Isovanillic acid (m. pt. 255°—257°C.) was obtained when hemipinic acid (1 part) was heated for 4 hours at 200°C. with dimethylaniline hydrochloride (2 parts). Experiments with aniline hydriodide and anisic acid showed that about two-thirds of the methyl radical split off was liberated as methyl iodide; the remaining one-third served to methylate some of the aniline.—E. W. L.

*Benzoylene-anthranil and bisanthranils and anthraquinone-azides.* A. Schaarschmidt. Ber., 1916, 49, 1632—1637.

ANTHRAQUINONE diazonium salts combine with sodium azide to form anthraquinone-azides. The azide from the 2-type of anthraquinone compound is stable in boiling water but the product of the 1-derivative readily loses two atoms of nitrogen yielding a pure, finely crystalline and stable compound, 3,4-benzoyleneanthranil, m. pt. above 300°C. Similarly from 1,5-diamino-anthraquinone there is obtained the corresponding bisanthranil derivative and from 1,4-diamino-anthraquinone the isobisanthranil derivative, reddish brown powders both giving strongly fluorescent solutions. Anthraquinone-2-azide, which is stable to boiling water, is a colourless powder crystallising from acetic acid in yellow needles, m. pt. 160°C. and decomposed on warming with strong sulphuric acid into hydroxyaminoanthraquinone.—J. F. B.

*Manufacture of gasoline and benzene-toluene from petroleum and other hydrocarbons.* Rittman and others. See IIa.

*The time factor in the formation of aromatic hydrocarbons from a paraffin base oil.* Egloff and Twomey. See IIa.

*Thermal decomposition of the ethane-propane fraction from natural gas condensate.* Zanetti and Leslie. See IIA.

*Fifty-second annual report on alkali, etc., works, by the Chief Inspector.* 1915. See VII.

*Coumarone resin and its uses.* Ellis and Rabinovitz. See XIII.

*Hydrogenation of heterocyclic compounds.* Skita and Brunner. See XX.

#### PATENTS.

*Sulphonation of organic compounds.* A. Heine-mann, Birmingham. Eng. Pat. 12,260, Aug. 25, 1915.

THE sulphonation of aromatic compounds can be carried out with weaker acid, in a shorter time, and without carbonisation, if a small quantity of iodine be added. *Example.*—146 grms. of sulphuric acid, 70 grms. of benzene, and 0.25 gm. of iodine are heated and stirred together under a reflux condenser for five hours. The whole of the benzene will then have been converted into benzenemono-sulphonic acid. The iodine can be recovered by adding water to the product and filtering.—F. Sp.

*Toluene; Production of*—W. B. Sifton, and Harding Bros., Ltd. Fr. Pats. 479,295 and 479,296, July 17, 1915.

SEE Eng. Pat. 8886 of 1915; this J., 1916, 248.

*Toluene; Apparatus for production of*—W. B. Sifton. Fr. Pat. 479,297, July 17, 1915.

SEE Eng. Pat. 9437 of 1915; this J., 1916, 248.

#### IV.—COLOURING MATTERS AND DYES.

*Absorption of colouring matters by charcoal and silica.* E. Knecht and E. Hibbert. J. Soc. Dyers and Col., 1916, 32, 226—230.

A DETAILED account of the literature referring to the subject is given, and emphasis is laid on the fact that animal charcoal cannot be regarded as one form of the element carbon. The examination of charcoals which have been treated to remove or introduce nitrogen has shown that the nitrogen content has a direct influence on the absorption of Crystal Scarlet and Methylene Blue. The product obtained from pure silk, and activated by heating with potash, absorbed a considerable amount of Crystal Scarlet, and hence the sulphur present in animal charcoal is not responsible for its colour-absorbing properties. A sample of bone charcoal had not such a great absorptive power as a sample of blood charcoal, although the former contained a higher percentage of nitrogen; this is probably due to the condition of the nitrogen, and Glassner and Spida (this J., 1907, 1915) have suggested that cyanamino-compounds are present in animal charcoal. In accordance with the results of Glassner and Suida (this J., 1908, 803), it was found that the oxygen content of charcoal plays an important part in the absorption of Methylene Blue. Experiments on the dyeing of silica and silicic acid led to the same results as those of Suida (this J., 1904, 1144; 1907, 1236); powdered quartz does not absorb Methylene Blue, and the absorption of this dyestuff by calcined silica is due to the fact that the silica is capable of being hydrated in the air or in contact with the solution of dyestuff.—F. W. A.

*Tetramethyldiaminophenazine.* P. Karrer. Ber., 1916, 49, 1643—1644.

SYMMETRICAL tetramethyldiaminophenazine is a

violet-red dyestuff obtained in moderate yield by the oxidation of an equimolecular mixture of dimethyl-*p*- and -*m*-phenylenediamines by potassium bichromate in presence of dilute hydrochloric acid; the reaction is completed by heating to 80° C. The zinc salt is precipitated by the addition of zinc chloride and saturated sodium chloride solution and converted into the hydriodide, which may be recrystallised from dilute alcohol. There is no change of colour on the addition of alkali. This dyestuff is not suitable for use in biological investigations like the similarly constituted Methylene Blue.—J. F. B.

#### PATENTS.

*o*-[Hydr]oxyazo dyestuffs; Manufacture of direct — O. Imray, London. From Soc. Chem. Ind. in Basle, Switzerland. Eng. Pat. 12,250, Aug. 25, 1915.

DIRECT *o*-hydroxymono-, dis-, or poly-azo dyestuffs are obtained by coupling an *o*-hydroxydiazocompound of the benzene or naphthalene series with an *N*-substituted 2-amino-5-naphthol-7-sulphonic acid or 2-amino-5-naphthol-1,7-disulphonic acid (except an *N*-alkyl or *N*-aryl derivative), in some cases using simultaneously any aromatic diazo-compound; or with the unsubstituted acids mentioned above or any substitution product, in some cases using simultaneously another end component or a middle component capable of being further diazotised and any aromatic diazo-compound. (Reference is directed, in pursuance of Sect. 7, Sub-sect. 4, of the Patents and Designs Act of 1907, to Eng. Pat. 21,473 of 1910; this J., 1911, 1109.)—F. W. A.

*[Anthracene] vat dyes and process of making them.* A. Lüttringhaus, Mannheim, Assignor to Badische Anilin u. Soda Fabr., Ludwigshafen, Germany. U.S. Pat. 1,196,127, Aug. 29, 1916. Date of appl., Oct. 20, 1913.

SEE Fr. Pat. 403,508 of 1913; this J., 1914, 415.

#### V.—FIBRES; TEXTILES; CELLULOSE; PAPER.

*Paper-making materials [Tambookie grass and Papyrus] from South Africa.* Bull. Imp. Inst., 1916, 14, 163—167.

TAMBOOKIE grass (*Cymbopogon Nardus* var. *validus*) grows extensively in the Transvaal, particularly in the northern parts. The sample examined ranged in length up to a maximum of 5 ft. 6 in., with a diameter of about  $\frac{1}{4}$  in. at the base. On digestion with caustic soda tambookie grass yields 37.1% of an easily bleachable pulp (dry pulp referred to air-dry material), showing an average length of fibre of 0.081 in., and is considered to be well adapted for paper-making and to have a value higher than that of Algerian esparto. Papyrus is found in the St. Lucia Bay districts of Zululand and samples of this reed have been compared with those obtained from East Africa and the Sudan. It is easily digested with caustic soda and gives a good bleaching pulp, but the yield of pulp from the South African variety is somewhat lower than from those obtained from other parts. In the case of both these South African materials, it is considered that export in the raw state would not be profitable on account of freight, but they could be converted into half stuff for export or for the manufacture of paper locally.—J. F. B.

## PATENTS.

*Fibrous compositions.* [*Roofing sheets.*] J. C. Woodley, Pelham Manor, N.Y., U.S.A. Eng. Pat. 8815, June 15, 1915.

FIBROUS material, e.g. waste paper or pulped stock, preferably in the moist condition, is steeped in or coated or sprayed with a hot liquid binding medium which subsequently becomes gummy on cooling. Generally, the binder may consist of a mixture of a natural or artificial flux oil or soft asphalt with harder asphalts such as gilsonite or hard pitch, for instance, a mixture of 88% of residuum oil, m.pt. 100°–120° F. (38°–49° C.), and 12% of grahamite. The saturated paper, cooled to a semi-solid consistence, is disintegrated into its ultimate fibres by forcing the mass repeatedly through perforated plates, so as to draw out the fibres between the surrounding elastic material. When the mixture is homogeneous it is subjected to pressure, e.g. by rollers, and formed into sheets, in which the fibres are completely coated with bituminous matter and felted together. The proportion of fibrous material should not exceed 50% of the mass and may preferably be between 5 and 30%.—J. F. B.

*Textile belts or the like; Process for impregnating* —with gutta-percha, balata, indiarubber or the like. E. C. R. Marks, London. From A./S. Roulunds Fabriker, Odense, Denmark. Eng. Pat. 101,127, Apr. 3, 1916. (Appl. No. 4882 of 1916.)

TEXTILE materials are treated with gutta-percha, balata, or rubber dissolved in suitable solvents, containing also 2–20% of a sulphonated oil to make the solution more fluid and assist penetration. The mixture may, if desired, also contain sulphur, preferably in solution, with a view to subsequent vulcanisation.—J. F. B.

*Stenciling fabric; Method of producing a* —. A. E. Strippel, New York. U.S. Pat. 1,194,899, Aug. 15, 1916. Date of appl., Nov. 22, 1912.

THE fabric is treated whilst protected from the light with a heated solution containing gelatin, glycerin, and potassium bichromate, in which the proportion of glycerin by weight exceeds that of the gelatin; it is then dried with exposure to light, treated with warm water, then with a 15% solution of calcium chloride, subjected to heat and pressure for drying, and finished.—J. F. B.

*Cellulose or paper-pulp from fibrous vegetable materials; Method of isolating or extracting* —and apparatus therefor. W. Raitt, London. Eng. Pat. 16,488, Nov. 23, 1915.

IN carrying out the process of fractional digestion, e.g., of bamboo, described in Eng. Pat. 15,779 of 1912 (see Fr. Pat. 453,307 of 1912; this J., 1913, 715), the operation may be reduced to two stages by extracting in an auxiliary vessel, those constituents which are soluble in water and in a dilute solution of caustic soda at a moderate temperature (100° C.), and subsequently removing the lignin by digestion with a stronger solution of caustic soda at a higher temperature (162° C.). The strength of the alkali used for the main (lignin) digestion may be such that the spent liquor contains sufficient unconsumed caustic soda to perform the preliminary extraction of a succeeding batch of material. The auxiliary vessel and the main digester may be so arranged that the charge of the former may be transferred to the latter, and the steam escaping from the main digester may be conducted into the auxiliary vessel to boil the contents at a lower pressure.—J. F. B.

*Paper pulp and the like [from sunflower stalks]; Process for the manufacture of* —. H. McCormack, Chicago, and E. W. McMullen, Kenosha, Wis., Assignors to F. Orth and J. Harbaugh, Indiana Harbour, Ind. U.S. Pat. 1,196,708, Aug. 29, 1916. Date of appl., Nov. 25, 1914.

CELLULOSE material, e.g. sunflower stalks, is dried and shredded, then digested in a solution containing 5% of sodium hydroxide, 10% of carbonate, 8% of sodium chloride, and 25% of sodium oxychloride (hypochlorite), calculated on the weight of the material, under a pressure of 80 lb. per sq. in. for about 10 hours. The digested material is beaten to a pulp in a pebble mill or the like, which may contain a dilute solution of permanganate.—J. F. B.

*Paper size and process of making same.* G. Muth, Butzbach, Assignor to Dr. Graf und Co., Neubabelsberg, Germany. U.S. Pat. 1,194,866, Aug. 15, 1916. Date of appl., Jan. 25, 1916.

AN artificial resin obtained from coal tar (coumarone resin) is melted with natural resin or a saponifiable fat until frothing has ceased, and the mixture boiled with an alkali until a uniform emulsion is produced.—J. F. B.

*Paper; Method and apparatus for sizing [surface-starching]* —. H. M. Wheelwright, Ware, Mass. U.S. Pat. 1,195,888, Aug. 22, 1916. Date of appl., July 22, 1915.

THE paper is led through a series of wet-presses and while passing between the last pair of press rolls a size composed of a soluble starch compound or "feculose" is applied to both sides of the moist web of paper by means of the press rolls, which transfer the starch solution to the paper.—J. F. B.

*Wool-scouring and analogous liquors; Concentration of* —and recovery of the grease and alkaline substances present therein. E. V. Chambers, T. C. Hammond, and G. G. Jarman. Fr. Pat. 478,041, May 8, 1915.

SEE Eng. Pat. 13,005 of 1914; this J., 1915, 276.

*Textile driving belts and the like; Impregnation of* —. Aktieselskabet Roulunds Fabriker. Fr. Pat. 479,333, Oct. 24, 1914.

SEE Eng. Pat. 101,127 of 1916; preceding.

*Cellulose esters; Preparation of new* —. Soc. Chim. Usines du Rhône (anc. Gilliard, P. Monnet, et Cartier). Fr. Pat. 478,436, Aug. 4, 1914.

SEE Eng. Pat. 10,822 of 1915; this J., 1915, 1086.

*Collodion [artificial silk]; Machines for spinning* —. H. de Chardonnet. Fr. Pat. 478,405, Aug. 1, 1914.

SEE Eng. Pat. 10,857 of 1915; this J., 1916, 538.

*Collodion [artificial silk] and like threads; Process and apparatus for denitrating, bleaching, dyeing, and otherwise treating* —. H. de Chardonnet. Fr. Pat. 478,404, Aug. 1, 1914.

SEE Eng. Pat. 10,858 of 1915; this J., 1916, 302.

*Paper pulp; Separation of metallic particles and other foreign matter from* —. A. J. Newell and R. J. Marx. Fr. Pat. 477,995, Mar. 12, 1915.

SEE Eng. Pat. 2865 of 1915; this J., 1915, 1138.

*Paper; Process and apparatus for pulping printed or unprinted* —and for removing ink from printed paper. General Waste Paper Recovery Co. Fr. Pat. 478,288, Mar. 20, 1915.

SEE Eng. Pat. 3702 of 1915; this J., 1916, 833.

*Paper-making machines, and manufacture of paper.* R. J. Marx. Fr. Pat. 478,839, Mar. 30, 1915.

SEE Eng. Pat. 3703 of 1915; this J., 1915, 1007.

*Pulp mills; Process of treating waste liquors from* —. E. L. Rinman, Harnäs, Sweden. U.S. Pat. 1,196,290, Aug. 29, 1916. Date of appl., Mar. 12, 1912.

SEE Fr. Pat. 441,186 of 1912; this J., 1912, 812.

## VI.—BLEACHING; DYEING; PRINTING; FINISHING.

*Absorption of colouring matters by charcoal and silica.* Knecht and Hibbert. See IV.

*Note on the cause of the pink colour observed in certain hypochlorite bleaching solutions.* Elledge. See VII.

### PATENTS.

*Textile materials; Scouring, bleaching, dyeing and the like machines for treating* —. F. F. Larivei, Bradford. Eng. Pat. 11,583, Aug. 11, 1915.

IN machines of the type in which the textile materials are supported on rollers or frames independent of the vats containing the treating liquids, these vats are supported by vertical columns formed as racks having teeth on one side. By means of toothed wheels and gear operated from two shafts, constantly rotated in the same direction and brought into action by hand-controlled clutches, the vat may be either raised or lowered and caused to come to rest at any predetermined point by means of a stop motion actuated automatically. —J. F. B.

*Bleaching process.* H. R. Anders and M. E. U. Schoedler, Perth Amboy, N.J., Assignors to The Roessler and Hasslacher Chemical Co., New York. U.S. Pat. 1,195,325, Aug. 22, 1916. Date of appl., Mar. 30, 1912.

THE container, which is divided into compartments, is packed in a horizontal position with the goods to be bleached, and is then inserted vertically in the vat; the dividing partitions prevent vertical displacement of the material. Bleaching liquor is passed through the goods in alternate directions until the desired result is attained. —F. W. A.

*Dyeing fabrics; Apparatus for* —. H. L. Quick, New York. U.S. Pat. 1,195,606, Aug. 22, 1916. Date of appl., July 30, 1914.

THE roll of fabric is carried by a rotating cylindrical frame, and the ends of the roll are closed by flanges having concentric circular grooves on the faces which abut against the ends of the roll. Dye liquor is supplied through a central perforated tube, which extends through the frame. —F. W. A.

*Dyeing machines.* J. Benosch, Assignor to Klauder-Weldon Dyeing Machine Co., Amsterdam, N.Y. U.S. Pats. (A) 1,195,648 and (B) 1,195,647, Aug. 22, 1916. Dates of appl., (A) May 11, and (B) June 9, 1914.

(A) A DYEING machine is provided with a rotary carrier having series of concentric inner and outer stick sockets and an independently rotating slide for locking simultaneously the sticks in a number of the sockets of one of the series. (B) A dyeing machine has a circular rotary carrier provided with means for supporting a pair of sticks oppositely disposed with respect to their ends, a locking member which fixes the pair of sticks simultaneously in working position, and also an arrangement which allows of the lateral removal or insertion of the sticks individually or collectively. —F. W. A.

*Weighting silk; Process of* —. Schmid frères, Fr. Pats. 479,312 and 479,316, July 19, 1915. SEE Ger. Pats. 287,754 and 291,009; this J., 1910, 174, 596.

*Sericin soap substitute for silk dyeing; Manufacture of* —. Schmid frères. Fr. Pat. 479,304, July 19, 1915.

SEE Eng. Pat. 100,169 of 1916; this J., 1916, 734.

*Dyeing silk in a foam bath.* Schmid frères. Fr. Pat. 479,726, Sept. 13, 1915.

SEE Eng. Pat. 100,336 of 1916; this J., 1916, 630.

*Dyeing fabrics, etc.; Method and apparatus for* —. Bradford Dyers Assoc., Ltd., and E. J. Wilkinson. Fr. Pat. 479,390, July 27, 1915.

SEE Eng. Pat. 17,215 of 1914; this J., 1915, 902.

*Producing bronze kid [leather].* Eng. Pat. 101,109, See XV.

## VII.—ACIDS; ALKALIS; SALTS; NON-METALLIC ELEMENTS.

*Alkali, etc., works; Fifty-second annual report on* — by the Chief Inspector. *Proceedings during the year 1915.* 100 pages. Price 2s.

THE number of registered works in England, Ireland, and Wales was 1372, including 63 "alkali works," and in Scotland 170, making a net increase of 16 for the United Kingdom compared with 1914. The increased activity is associated largely with the manufacture of chemicals used in production of munitions of war, and with the distillation of tar. The general average figures for the escape of acid gases vary, in most classes of works, but slightly from those for the two previous years. In the present report a differentiation is made between smelting works and other kinds of works, in regard to the acidity of chimney gases: for smelting works the general average acidity was 3.056 grains SO<sub>2</sub> per cb. ft.; for other works, 0.719 grain per cb. ft.; and for all works, 1.059 grains per cb. ft. There were three cases of contravention of provisions of the Act, but in view of the exceptional conditions no proceedings were taken. In two cases back fees were accepted in lieu of taking proceedings in regard to non-registration of processes. *Alkali and copper (wet process) works.* The production of hydrochloric acid was hampered by difficulty in obtaining sulphuric acid, and the difficulty was only partly overcome by an increased use of nitre cake in the salt-cake furnaces; in some districts the supply of hydrochloric acid was insufficient to meet the demand. The use of mechanical furnaces in connection with the extraction of copper by the wet process made further progress, and in one works an improved form of packing for the condensers was used, which is more readily washed than coke packing and shows less tendency to choke and cause interference with the draught on the furnaces. Efforts to increase the production in sulphuric acid works by using larger quantities of pyrites resulted in leaving a larger proportion of residual sulphur in the burnt pyrites than formerly and in consequence of this the acidity of the copper works' chimney gases increased.

In one works where hydrochloric acid is made from salt and nitre cake, the presence of undecomposed sodium nitrate in the nitre cake caused trouble owing to the formation of chlorine, which partly passed the condenser and escaped from the chimney. The difficulty was overcome by the addition of sulphur to the charge.

**Smelting works.** There was some increase in the utilisation for the manufacture of sulphuric acid of the gases from furnaces for the calcination of zinc sulphide ores, but regret is expressed that considerable extensions of calcining plant for zinc ores were erected during 1915, and further extensions are under construction, which will not permit of the utilisation of the gases. The use of electrical methods to aid in the deposition of dust and fume is to be tried in one works.

**Cement works.** Reference is made to the presence of potassium compounds in the flue-dust from cement kilns.

**Sulphuric acid works** continued working under great pressure; nevertheless the general average acidity of the escaping gases was only 1.137 grain  $\text{SO}_3$  per cb. ft., as compared with 1.191 grain in 1914. A mechanical washer for recovery of nitrous gases from the residual gases leaving the last chamber has been installed in one works with successful results, and is to be introduced in other works. This method of washing presents advantages over the use of large absorption towers, especially towers packed with coke. Of 338 Glover towers in the United Kingdom, 130 are packed with flints, 127 with bricks, 28 with bricks and flints, 23 with rings, 16 with bricks or tiles and rings, 8 with tiles, and 6 with bricks and tiles; and of 140 Gay Lussac towers, 269 are packed with coke, 53 with bricks, 43 with glass, 25 with rings, 17 with tiles, 10 with bricks and tiles, 8 with rings and coke, 7 with bricks or tiles and coke, 4 with rings and tiles, 3 with Lunge-Rohrmann tiles,

and 1 with balls. Two deaths occurred as a result of gassing by nitrous fumes during the cleaning of a tank railway waggon and a tank used for storing Glover tower acid respectively, and in view of the repeated occurrence of such fatalities a re-statement of the precautions which should be taken (see this J., 1913, 787) was embodied in a circular letter which was sent to owners of sulphuric acid works. The manufacture of sulphuric acid by the contact process was carried on to the full capacity of existing plants, and several extensions of plant were brought into operation. Extensive additions were also made to plants for the concentration of acid and numerous new installations were erected. In this connection much trouble was caused through inefficient design and construction of plant, especially with the cascade system and, to a lesser extent, with the Gaillard tower system. Less trouble was experienced with the Kessler system, but the increased use of plant of this type was interfered with very seriously owing to lack of the necessary material. The Kessler type of plant seems less suitable for certain kinds of impure acid which are concentrated for use a second time. For the efficient and satisfactory operation of the cascade type of concentrating plant: (1) there must be a greater draught in the flue leading the vapours and gases to the condensers than in the flue leading the fire gases to the chimney; (2) local overheating must be avoided; and (3) adequate means for condensing the acid vapours must be provided. The following tables have been compiled from experience gained in the use of the cascade system of concentration:—

#### Cascade plant and condensers.

Basins of silica, "ironac," "narki," and "tantiron," with preheaters.

Acid feed strength.	Number of basins.	Output, tons of acid (166°–169° T.) per 24 hours.	Water and acid evaporated per 24 hours. Tons per 100 basins.			Packing in condenser.			
			Loss of strong acid assumed to be:			Per basin.		Per ton of strong acid made.	
			NIL.	5%	15%	Volume, cubic feet.	Sectional area, sq. feet.	Volume, cubic feet.	Sectional area, sq. feet.
165° T.	727	61.5 (= 1.60 cwt. per basin)	4.5	5.1	6.4	6.5	Coke packing. 1.6	77	18
123° T.	1440	112 (= 1.55 cwt. per basin)	3.1	3.6	4.7	8.2	0.7	105	10
136° T.	40	4 (= 2 cwt. per basin)	2.7	3.3	4.6	6.2	1.2	62	12
147° T.	100	15 (= 3 cwt. per basin)	2.9	3.8	5.5	7.5	—	50	—
129° T.	40	2.5 (= 1.25 cwt. per basin)	2.5	2.9	3.8	5.0	Ring packing. —	76	—

#### Cascade plant and condensers, with preheaters.

Acid feed strength.	Description of plant.	Output of acid.		Nature.	Packing in condensers.			
		Tons per 24 hours.	Strength ° T.		Per basin.		Per ton of strong acid made.	
					Volume, cubic feet.	Sectional area, sq. feet.	Volume, cubic feet.	Sectional area, sq. feet.
110° T.	3 Tantiron pans and basins	5	168	Coke	—	—	43	7
120° T.	12 Tantiron dishes (3 ft. diam.)	12	166	Bricks and tiles	—	—	30	—
129° T.	80 Silica basins and 2 iron "pots" (8 ft. × 3 ft.)	14	168	Rings	—	—	15	—
135° T.	" Webb " plant—30 vessels	4.5	168	Coke and brick	14.5	15.1	96	101

**Chemical manure works.** The scarcity of sulphuric acid interfered very seriously with production in some districts. The quantities of the more important manure materials imported into the United Kingdom during the past three years, were:—

	1915.	1914.	1913.
	tons.	tons.	tons.
Guanos .....	20,720	39,285	25,548
Mineral phosphates .....	574,639	553,806	539,016
Sodium nitrate .....	152,158	171,910	140,926

The exports of ammonium sulphate in 1915 amounted to 294,000 tons, as compared with an estimated home consumption (for all purposes) of 128,000 tons, the corresponding figures for 1914 being 314,000 tons and 100,000 tons respectively.

**Sulphate and muriale (chloride) of ammonia, and gas liquor works.** The quantity of ammonia (expressed as tons of sulphate) recovered as a by-product in the United Kingdom was:—

	1915.	1914.	1913.
Gas works .....	173,675	175,930	182,180
Iron works .....	15,142	16,008	19,956
Shale works .....	59,826	62,749	63,061
Coke oven works .....	146,406	137,430	133,516
Producer gas and carbonising works (bone and coal) ..	33,218	34,295	33,605
Totals .....	426,267	426,412	432,618

**"Direct" process for manufacture of sulphate of ammonia; and storage of ammoniacal liquor.** See under II A., page 1001.

**Nitric acid works.** Many new works were erected and large additions were made to some existing works. Conditions were satisfactory in works in which nitric acid was made from sodium nitrate, but left much to be desired in those works in which the acid was recovered by treatment of nitrous fumes; improvements have, however, been effected and the conditions are becoming more satisfactory. No works came under inspection in which nitric acid was made by a synthetic method, although in other countries where cheap power is available, large quantities are obtained by such means.

**Chlorine works.** Two additional works were started. In one works the local diffusion of dust in the operation of "knocking down" bleaching powder when packed in casks has been very largely reduced by placing over the cask a wooden hoop covered with cloth.

**Tin plate flux works.** An investigation of the efficiency of the method used for the recovery of hydrochloric acid and metallic fumes evolved during the operation of calcining scruff and flux skimmings showed that considerable quantities of the metallic fumes escape condensation. It is suggested that improvement, without undue complication of plant, might be effected by:—(1) A lower working temperature at the furnace; (2) provision of a condensing flue of larger sectional area, preferably one with sumps and baffles; (3) regulation of draught at the chimney end of the flue instead of at the furnace; (4) cooling of the gases by bringing them into contact with water soon after entering the flue, so as to obtain the full cooling effect due to evaporation. About 63 gallons of water would be required to reduce the temperature of 100,000 cu. ft. of gases (at 0° C. and 760 mm.) from 400° to 200° C., and the best method would be to introduce atomised water.

**Picric acid works.** New works of large productive capacity have been erected and large extensions

made to existing works. In some works there was too great an emission of noxious gases, but improvement is being gradually effected.

**Tar works.** The number of works increased by 43, largely due to the extending practice of preparing tar for road surfacing and light oils rich in benzol and toluol from crude tar. The amount of tar distilled in the United Kingdom is given as 1,311,383 tons in gas works and 163,927 tons in other works, the corresponding figures for the amount of pitch produced being 669,489 and 80,907 tons respectively.

**Industrial scientific control.** Little or no change was observed as regards mutual effort to improve working methods or as regards the fuller appreciation of the value of the properly trained technical chemist. There are numerous instances where individual firms keep themselves informed regarding developments, but co-operative action is needed as a means towards general increased efficiency.

**Scotland.** The production of ammonium sulphate was less than in 1914, chiefly owing to diminished output from shale works. The comparative figures (those for 1914 being given in brackets) are:—Gas works, 22,861 (22,362) tons; iron works, 14,091 (14,703); shale works, 58,826 (62,749); bone works, and producer gas, coke and carbonising works, 22,400 (22,244); total, 118,178 (122,058) tons.

The amount of pyrites burned was 144,946 tons (130,435 tons in 1914), and of bones and phosphates dissolved, 64,892 tons (61,712 tons in 1914). 70,719 tons of pitch was produced in gas works and 73,292 tons in other works, the corresponding figures for the amount of tar distilled being 135,517 and 149,584 tons respectively.—A. S.

**Felspar; Decomposition of—**for the commercial production of potassium salts. B. Neumann and F. Draibach. Z. angew. Chem., 1916, 29, 313—319, 326—331.

LABORATORY experiments were made in order to ascertain the yields of water-soluble potassium compounds obtainable by heating felspar with various substances (1) in the dry state, (2) in the presence of water in an autoclave, and (3) to very high temperatures in order to volatilise the potassium compounds. Better yields were obtained by the dry method than by heating in an autoclave, and the most suitable reagents were found to be lime mixed with magnesium chloride or calcium chloride. From a mixture of equal quantities of commercial ground felspar, lime, and calcium chloride, over 95% of the potash was recovered after heating for 3 hours at 650° C., but with the proportions recommended by Cushman and Coggeshall (this J., 1915, 79), i.e., 20% each of lime and calcium chloride, together with water to form the mass into lumps, the maximum yield obtained in 1½ hours was 47.4% at 750° C. Above 750° C. the amount of potash volatilised steadily increases. The economic aspects of the extraction of potash from seaweeds, alunite, felspar, etc., are discussed, and it is concluded that under normal conditions none of these processes will be able to compete successfully with the German potash industry.—A. S.

**Leucite; Solubility of—**in sulphurous acid. J. Schroeder. J. Ind. Eng. Chem., 1916, 8, 779—780.

A SAMPLE of finely ground leucite was sifted into different grades, and the different fractions shaken with a saturated solution of sulphurous acid, left overnight, and then filtered. From 16.4 to 26.2% of the leucite was dissolved, and the solution contained from 41.7% to 76.4% of the total potash present. It is suggested that the porous leucite rock of the Leucite Hills, Wyoming, might be leached with sulphurous acid obtained from the waste gases of the smelting plants in

Utah, Colorado, and Montana. The amount of potash in the rocks of the Leucite Hills region has been estimated at 197,349,600 tons.—A. S.

*Hypochlorite bleaching solutions; Note on the cause of the pink colour observed in certain*—  
H. G. Elledge. J. Ind. Eng. Chem., 1916, 8, 780—781.

SODIUM hypochlorite solutions prepared from bleaching powder and so-called neutral washing powder (a mixture of sodium carbonate and bicarbonate) are invariably pink. If normal sodium carbonate or sulphate is used, a green solution is obtained, which becomes pink when agitated with sodium bicarbonate. Tests in which small quantities of manganous sulphate or of ferric chloride were added, indicated that the coloration is not due to sodium ferrate, as has been suggested, but to sodium permanganate, and this was confirmed by comparison of the absorption spectrum of the pink solution with that of a solution of permanganate. The manganese is derived from the bleaching powder.—A. S.

*Magnesium sulphide; Preparation of pure and its phosphorescence.* E. Tiede. Ber., 1916, 49, 1745—1749.

MAGNESIUM sulphide prepared by the method of Mourlot (this J., 1898, 881) was found to contain only 8% of sulphur instead of 56.8%, the theoretical figure. Reichel's process of heating magnesium in a current of hydrogen followed by a current of the same gas mixed with sulphur vapour, gave a product containing 30—50% of sulphur. Magnesium sulphide made in this way was purified by heating it in a highly evacuated quartz tube to 600°—700° C. for two hours, whereby the excess of metal was volatilised. It was also purified by boiling it (10 grms.) with fresh, absolute ether (100 c.c.), ethyl iodide (10 grms.), and a crystal of iodine for 3 hours, moisture being rigorously excluded. The metal dissolves in the alkyl halide whilst the sulphide is unaffected. The purified sulphide was then washed with ether and dried in a vacuum desiccator placed in the water bath. Analysis showed it to be pure and the spectroscopic proved the absence of alkaline-earth metals. It had a reddish-white colour, was amorphous, and feebly luminescent after exposure to daylight or to an arc light. The luminescence is apparently best excited by rays of long wavelength: radium-, X-, and ultra-violet rays did not excite it. When exposed to direct cathode rays, magnesium sulphide shows a bright blue and red fluorescence and a feeble after-glow.—E. H. T.

*Barium sulphate; Laboratory experiments concerning the reduction of*—to barium sulphide. A. E. Wells. J. Ind. Eng. Chem., 1916, 8, 770—777.

BELOW 750° C. the reduction of barium sulphate by carbon or by reducing gases was too slow to be of use commercially. The maximum yield of sulphide was obtained at the highest temperatures employed, i.e., at about 1000°—1150° C. Taking both consumption of carbon and yield of sulphide into account, the best results were obtained with 15—18% of carbon when reduction was effected in a muffle furnace. When reduction was effected in a direct-fired furnace (a rotary cement kiln, a shaft furnace, or a multiple-hearth roasting furnace), in which the material came in direct contact with reducing gases or products of combustion, the proportion of reduction products insoluble or sparingly soluble in water was higher than when reduction was effected in a muffle furnace. For example, in a muffle furnace, with 15.5% of carbon, a yield of 96% of water-soluble sulphide was obtained at 1050° C. and 99% at 1150° C., whereas the best results in a direct-fired furnace were 85 to 87% of water-soluble sulphide.

The amount of insoluble reduction products was less when reduction was effected rapidly at high temperatures (above 1000° C.) than when lower temperatures were used with longer duration of heating.—A. S.

*Nickel in cobalt salts; Detection of*—A. R. Middleton and H. L. Miller. J. Amer. Chem. Soc., 1916, 38, 1705—1711.

By the following method considerably smaller quantities of nickel can be detected than has been possible hitherto, and with a smaller consumption of dimethylglyoxime, even in presence of relatively large quantities of cobalt. The solution containing nickel and cobalt (about 10—15 c.c.) is treated with 10% potassium cyanide solution until the precipitate which forms at first just redissolves, and the solution is heated and rotated for 5 mins. after the colour changes from greenish-brown to pale yellow. It is then diluted to 50 c.c. with water at 85° C., and treated with 1 c.c. of a 1% alcoholic solution of dimethylglyoxime, after which 1% silver nitrate solution is added, drop by drop, with constant stirring, until a permanent precipitate is produced. The presence of nickel is indicated by a pink colour, which appears only after some hours when the quantity of nickel is very small. It is possible to detect 0.02 mgrm. of Ni in 1 hour and 0.002 mgrm. in 24 hours. The effect of the silver nitrate is to precipitate the cyanide ion as silver argenticyanide and promote decomposition of the nickelocyanide ion, thus increasing the concentration of nickel ions, whilst the cobaltcyanide ion remains practically unaffected. The increased sensitiveness of the test is probably due to increased concentration of nickel ions owing to adsorption by the precipitated silver argenticyanide. A similar effect is produced if silver chloride be precipitated in the mixture, but precipitation of a positive colloid, such as aluminium hydroxide, has no effect.—A. S.

*Manganous to manganic salts; Oxidation of*—by nitrous acid. W. Prandtl. Ber., 1916, 49, 1613—1614.

WHEN a cold solution of a manganous salt is acidified with excess of strong hydrochloric acid and a few drops of sodium nitrite solution added, or when cooled strong hydrochloric acid is mixed with a little nitrite solution and a few drops of a solution of manganous salt added, the liquid darkens to an intense brownish-yellow, owing to the formation of manganic chloride. When a neutral solution of a manganous salt is mixed with excess of neutral sodium nitrite, the addition of oxalic acid produces an intense cherry red coloration, owing to the formation of manganic oxalate. This reaction is extremely sensitive and may be used for the detection of small quantities of manganese in presence of considerable quantities of iron.—J. F. B.

*Chromous salts; Electrolytic preparation of*—from chromic salts, and some new salts of divalent chromium. W. Traube and A. Goodson. Ber., 1916, 49, 1679—1691.

SOLUTIONS of chromous salts were obtained by the electrolytic reduction of chromic salts in a divided cell with prepared lead electrodes (Tafel, this J., 1900, 909) and a current density of 2.5 ampères per sq. dm. The reduction was followed quantitatively by measurements of the hydrogen liberated at the cathode and in a voltmeter included in the same circuit, and also by iodometric determinations of the chromous salt produced, and it was found that the highest current yields (from 70 to 86%) were obtained by the use of violet chromic salts in concentrated solution containing about 1% of mineral acid. The last stages were, however, slow and the current yields very low, when electro-



lysis was continued until complete reduction of the chromic solution was attained. The green chromic salts were reduced with greater difficulty than the violet salts in equal concentrations, but in the initial stages of the reduction and when a complete reduction is not desired, this is compensated for by their greater solubility. In all cases it was necessary to protect the chromous solutions from the oxidising action of the air either by entirely closing the cathode compartment, or else by covering the surface of the liquid with a layer of petroleum spirit. From the chromous salt solutions prepared in this way chromous formate,  $\text{Cr}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ , was obtained as a red crystalline powder by the addition of an excess of sodium formate. In a similar way chromous glycolate was prepared. Both these salts can be recrystallised from water in the absence of air. Sodium malonate precipitates in blue needles a double salt, sodium chromous malonate,  $\text{Na}_2\text{Cr}(\text{C}_2\text{H}_3\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ , but in presence of an excess of chromous chloride and free malonic acid the red, almost insoluble, and comparatively stable, chromous malonate is formed.—G. F. M.

*Chromous salts; Behaviour of — towards acetylene, and the reducing action of salts of divalent chromium.* W. Traube and W. Passarge. Ber., 1910, 49, 1692—1700.

By agitation with acid solutions of chromous chloride, prepared by the reduction of chromic chloride with zinc and hydrochloric acid, acetylene was converted quantitatively into ethylene. Provided sufficient zinc and hydrochloric acid were present, a very small quantity of chromium salt acted catalytically in the above reaction, as was shown by the fact that in its absence no appreciable alteration of the acetylene was observed, nor could it be successfully replaced by other chlorides, such as ferrous or manganous chloride. That the reaction stops at the ethylenic stage, is probably due to physical conditions, for in other cases, such as malic and fumaric acids, and phenylpropionic and cinnamic acids, complete reduction to the saturated compounds was brought about by chromous chloride. Alkaline chromous chloride solutions energetically and quantitatively reduced nitric acid and nitrates, and also hydroxylamine, to ammonia, and the reducing agent may therefore be advantageously employed for the determination of these substances as ammonia. In acid solution the reaction is not quantitative, and the reduction of nitrites under all conditions gave low results, which is probably to be ascribed to the formation, and subsequent decomposition, of ammonium nitrite. Oximes, as for example benzaldoxime, in alkaline solution, are reduced by chromous solutions to amines.—G. F. M.

*Cæsium and rubidium; Separation of — by the fractional crystallisation of the aluminium and iron alums, and its application to the extraction of these elements from their mineral sources.* P. E. Browning and S. R. Spencer. Amer. J. Sci., 1910, 42, 279—281.

A SOLUTION obtained from the decomposition of lepidolite by heating with fluor spar and sulphuric acid was freed from calcium sulphate and evaporated until crystals of the mixed alums appeared. The mother liquor was separated, further evaporated, the crystals separated, and so on. The first crystals formed were dissolved, recrystallised, the liquor added to the second crop, and the process continued as in ordinary fractional crystallisation. After about seven crystallisations, the crystals in the first vessel consisted of pure cæsium alum, but twenty-two crystallisations were necessary to obtain the more soluble rubidium alum in a state of purity. Better results were obtained with cæsium and rubidium iron alums; the solution of the mixed alums from lepidolite was treated with

ammonia, the aluminium hydroxide separated by filtration, the filtrate evaporated, and mixed with crystals of ammonium ferric alum. The mixture was warmed, then cooled and allowed to crystallise; the first crop of crystals consisted of pure cæsium iron alum and contained no rubidium. For the extraction of cæsium from pollucite, the mineral was decomposed with hydrochloric acid, the silica separated, and the acid solution poured on ammonium aluminium alum, and warmed. Cæsium alum separated on cooling; the crystals were twice recrystallised and then found to be pure; the remainder of the cæsium was obtained by a few crystallisations of the mother liquors.

—W. P. S.

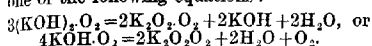
*Colloidal arsenious sulphide; Coagulation of — by electrolytes, and its relation to the potential difference at the surface of the particles.* F. Powis. Chem. Soc. Trans., 1910, 109, 734—744.

FIVE c.c. of a colloidal solution of arsenious sulphide, containing 11 grms. per litre, was mixed with 5 c.c. of electrolyte solution of the required concentration. Experiments made with barium chloride of concentrations varying from 0.3 to 0.8 millimol. per litre, have shown that there is no definite concentration above which coagulation occurs almost immediately, but below which no coagulation occurs. The mixture containing 0.4 millimol. slowly changed, so that after 8 days nearly all the arsenious sulphide had been precipitated. If equal quantities of colloid and electrolyte solutions are mixed, the progress of coagulation and settling is influenced but little by the subsequent shaking of the tube, unless the electrolyte concentration is near that which causes immediate turbidity, but not immediate coagulation and settling, e.g., 0.5 millimol. in the case of barium chloride. The relation between the stability and the potential difference at the surface of the particles was determined with electrolytes, in which the concentrations were such that the colloid has the same stability as in the presence of 0.5 millimol. of barium chloride, the electrolytes being hydrochloric acid 30 millimols., potassium chloride 40 millimols., aluminium chloride 0.05, and thorium nitrate 0.05 to 0.1 millimol. per litre. The results obtained were very constant in the cases of barium and aluminium chlorides and thorium nitrate, varying from  $-0.024$  to  $-0.027$  volt, but in the cases of potassium chloride and hydrochloric acid were much higher, viz.,  $-0.044$  and  $-0.05$  volt. A critical potential difference appears to determine the stability or instability of a colloidal solution, so far as barium and aluminium chlorides and thorium nitrate are concerned, but the behaviour of potassium chloride has suggested that electrolytes also exert a kind of salting-out effect. The lack of sharpness in the coagulation concentration is explained as being due to the critical value of the potential difference being slightly different for particles of different size.—B. N.

*Ozonates; The so-called alkali —.* W. Traube. Ber., 1910, 49, 1670—1679.

THE so-called ozonates, coloured compounds formed superficially on the alkali hydroxides by the action of ozone, if decomposed by water or a dilute acid immediately after their formation, give up all the absorbed oxygen almost completely as gas, slight traces only of hydrogen peroxide being formed. On keeping for several days, and more rapidly still if water is not rigidly excluded, the compounds lose their colour, and on decomposition as above give oxygen and hydrogen peroxide in practically molecular proportions, indicating complete conversion into alkali tetroxides. A second decomposition proceeds at the same time as this conversion into tetroxide

in that the "ozonates" part with molecular oxygen, and revert to hydroxides. At 0° C. these changes occur more slowly, and to the advantage of the tetroxide formation, so that by repeated ozonisation it was possible to prepare a substance containing 10% of potassium tetroxide. Regarding the constitution of these ozonates, the author prefers to consider them as molecular compounds (or compounds of the second order), formulating them either as  $\text{KOH}\cdot\text{O}_2$ , or  $(\text{KOH})_2\cdot\text{O}_2$ , the tetroxides being  $\text{K}_2\text{O}_2\cdot\text{O}_2$  or  $\text{K}\cdot\text{O}\cdot\text{O}\cdot\text{K}\cdot\text{O}_2$ , and thereby offering some explanation why the excess oxygen is evolved in both cases as molecular oxygen and not as active oxygen, as might have been expected from such highly oxidised substances. The conversion of the ozonates into tetroxides would be accordingly represented by one of the following equations:—



—G. F. M.

*Azides of alkali and alkaline-earth metals; Decomposition of — in high vacuo. Preparation of pure nitrogen.* E. Tiede. Ber., 1916, 49, 1742—1745.

THE azides of the alkali and alkaline-earth metals were decomposed by heating them in Jena glass tubes of 10 mm. diameter immersed in a paraffin or sand-bath, and evacuated with a Gaede mercury pump. A small sparking-tube was let in at the side of the Jena tube in order that the gas evolved might be examined spectroscopically. The azides were prepared by neutralising 5% hydrazoic acid (azolumide) with the metallic hydroxide, and were purified by re-crystallisation, and dried *in vacuo* over sulphuric acid. The temperatures at which the azides began to decompose and at which the evolution of nitrogen became regular were as follows: sodium 330° and 280° C., potassium 320° and 360° C., rubidium 260° and 310° C., cesium 290° and 300° C., calcium 110° and 100° C., strontium 140° and 110° C., barium 160° and 120° C. The alkali metals formed lustrous, silver-white mirrors on the sides of the tubes, but the sodium mirrors had a yellowish tinge. The alkaline-earth metals were first left in the bottom of the tube as very finely divided, blackish powders, which were volatilised—and also formed mirrors—when the temperature was raised. When the powders were heated in a slow current of air they ignited without loss of colour and the smell of ammonia afforded evidence that nitrides were present. When heated further in the Bunsen flame, they ignited anew and were converted into pure oxides. With the exception of lithium azide, the azides used did not explode when heated. In every case the nitrogen evolved was found to be of exceptional purity.—E. H. T.

*Direct process for the manufacture of sulphate of ammonia, and the storage of ammoniacal liquor.* Curphey. See IIA.

*Volumetric determination of hydrogen by oxidation with activated chlorate solution. Removal of carbon monoxide by means of mercuric chromate.* Hofmann. See IIA.

*Retardation by carbon monoxide of the oxidation of hydrogen in the chlorate pipette, a contribution to the knowledge of contact poisons.* Hofmann and Schibsted. See IIA.

#### PATENTS.

*Acids; Method of, and apparatus for, concentrating —.* T. C. Oliver, Assignor to Chemical Construction Co., Charlotte, N.C. U.S. Pat. 1,195,075, Aug. 15, 1916. Date of appl., Mar. 22, 1916. Hot gases are passed over the surface of the acid,

and then upwards through a tower packed with impervious material down which more acid flows into the main body. Jets of air are passed through the acid to agitate it, and to expose fresh surfaces to the hot gases.—E. H. T.

*Oxides of nitrogen; Production of — and catalysts to be employed therein.* J. Y. Johnson, London. From Badische Anilin- und Soda-Fabrik, Ludwigshafen, Germany. Eng. Pats. (A) 7651, May 21, 1915; Addition to Eng. Pat. 13,848, June 8, 1914 (this J., 1915, 799) and (N) 13,298, May 21, 1915.

(A) IN the preparation of oxides of nitrogen by the method described in the chief patent, the catalyst may be composed of almost any metal or metallic oxide along with bismuth or its oxide. The best proportion of bismuth varies considerably. Particulars are given of the preparation of a copper-bismuth oxide, fireclay with a platinum-bismuth oxide, and a magnesium-bismuth oxide. (N) When noble metals are used in the catalyst, especially those of the platinum group, lead may be used instead of a part or the whole of the bismuth or of the tellurium specified in Eng. Pat. 13,297 of 1915.—B. V. S.

*Sodium bisulphite; Manufacture of —.* T. W. S. Hutchins, L. Hargreaves, and A. C. Dunningham, Middlewich. Eng. Pat. 10,556, July 21, 1915.

SODIUM bisulphite is prepared by the action of sulphur dioxide on hydrated sodium carbonate. The sulphur dioxide is generated by burning sulphur, and freed from oxygen and sulphur trioxide by means of hydroxides or carbonates or both of the alkali or alkaline-earth metals. It is then passed on to the sodium carbonate which is so arranged in a tower or other suitable vessel that the carbon dioxide generated by the reaction in the first layers passes on to the succeeding layers, converting them to the bicarbonate, so that the bulk of the reaction occurs between sulphur dioxide and the bicarbonate. By using the monohydrated carbonate or a mixture of soda crystals and soda ash to give the same amount of water as in the monohydrate, solid dry bisulphite is formed. If the decahydrate is used the liberated water serves to dissolve the bisulphite formed and a strong bisulphite solution is obtained. Any sulphur dioxide occluded in the solid bisulphite is driven out by passing through the mass the carbon dioxide-nitrogen mixture issuing from the reaction chamber.—B. V. S.

*Sodium pyrophosphate and active oxygen; Manufacture of products containing —.* O. Imray, London. From Soc. of Chem. Ind. in Basle, Switzerland. Eng. Pat. 15,749, Nov. 8, 1915.

IF 3 mol. proportions of hydrogen peroxide are caused to interact with 1 mol. of sodium pyrophosphate, a solid, dry product containing active oxygen equivalent to over 27% of hydrogen peroxide is obtained, and products containing less than this amount of active oxygen can be made by suitably reducing the proportion of peroxide employed. Powdered sodium pyrophosphate, dry or dissolved in water, is mixed with peroxide of the desired strength, and the solution is evaporated to dryness as quickly as possible either *in vacuo* or in a current of dry air; or, anhydrous pyrophosphate may be shaken or ground with peroxide in ethereal solution and the solvent removed by evaporation. To obtain products with a relatively low active oxygen content and in a dry state, anhydrous pyrophosphate is ground with aqueous hydrogen peroxide which contains only as much water as will combine with the phosphate. Similar products may be obtained by condensing steam containing hydrogen peroxide

upon the anhydrous salt. Instead of using the ordinary salt, acid pyrophosphate or the free acid may be decomposed, in presence of a solvent for hydrogen peroxide, by means of sodium peroxide or sodium percarbonate, and then, if necessary, peroxide added to bring the product up to the desired strength.—E. H. T.

*Potassium salt; Process of producing a — from insoluble silicates.* H. P. Bassett, Catonsville, Assignor to The Spar Chemical Co., Baltimore, Md. U.S. Pat. 1,194,464, Aug. 15, 1916. Date of appl., Mar. 8, 1915.

AN insoluble silicate containing potassium is mixed with a sulphate, e.g., sodium bisulphate, and a catalyst, e.g., a fluoride, and the whole is heated in a furnace to a red heat. The catalyst accelerates the action of liberated sulphur trioxide upon the silicate.—E. H. T.

*Alunite and the like; Treatment of —.* H. F. Chappell, Assignor to Mineral Products Corporation, New York. U.S. Pat. 1,195,655, Aug. 22, 1916. Date of appl., Sept. 23, 1913.

ALUM. alum stone, alum rock, or alunite is heated in a reducing atmosphere to a temperature between 650° and 1000° C. The excess sulphur over that required for the formation of potassium sulphate is driven off as such and is recovered. A residue of potassium sulphate and alumina is left, from which the former is separated by lixiviation.—B. V. S.

*Titanium compound; Method for producing —. Method of treating titanic oxide. Titanium compound.* A. J. Rossi and L. E. Barton, Niagara Falls, N.Y., Assignors to The Titanium Alloy Manufacturing Co., New York. U.S. Pats. (A) 1,196,029, (B) 1,196,030, and (C) 1,196,031, Aug. 29, 1916. Dates of appl., (A) Nov. 29, 1912, (B) Mar. 10, 1915, (C) Feb. 10, 1916.

(A) A substance containing titanic oxide ( $\text{TiO}_2$ ) and iron oxide is heated with a reducing agent, such as carbon, so as to form titanous oxide ( $\text{Ti}_2\text{O}_3$ ). The resulting melt is treated with sulphuric acid, titanous sulphate being formed, and the solution is then diluted and boiled to precipitate basic titanium sulphate. The addition of a little nitric acid to the dilute solution renders the precipitation more rapid and complete. (B) The substance containing titanic oxide is digested at 100° to 150° C. with about  $2\frac{1}{2}$  parts by weight of sulphuric acid to 1 part of titanic oxide, the resulting mass dissolved in water, the solution diluted and boiled to precipitate basic titanic sulphate. The iron present may be reduced to the ferrous state before the solution is boiled. (C) A new basic titanium sulphate is described containing less combined water than titanic oxide and less sulphuric anhydride than combined water.—B. V. S.

*Sulphuric acid; Concentration of —.* La Fabr. de Soic Artificielle de Tubize. Fr. Pat. 479,320, July 20, 1915.

SEE Eng. Pat. 10,386 of 1915; this J., 1916, 537.

*Salt; Process and apparatus for converting rock salt into table —.* L. W. Damman. First Addition, dated June 23, 1915, to Fr. Pat. 475,235, May 1, 1914.

SEE Ger. Pat. 291,265 of 1914; this J., 1916, 690.

*Salts from sea water; Extraction of —.* Y. I. A. Lalljee. Fr. Pat. 479,770, Sept. 17, 1915.

SEE Eng. Pat. 6678 of 1915; this J., 1916, 690.

*Ammonia; Extraction of — from ammoniacal liquor.* British Coke Ovens, Ltd. Fr. Pat. 477,962, Mar. 9, 1915.

SEE Eng. Pat. 6061 of 1914; this J., 1915, 787.

*Sodium carbonate; Apparatus for producing —.* M. Spazier. Fr. Pat. 477,964, Mar. 9, 1915.

SEE U.S. Pat. 1,127,691 of 1915; this J., 1915, 282.

*Alkali carbonates; Recovery of — from alkali nitrates obtained by absorbing nitrous gases with alkali carbonates.* Norsk Hydro-Elektrisk Kvaelfstofaktieselskab. Fr. Pat. 478,976, June 8, 1915.

SEE Eng. Pat. 8270 of 1915; this J., 1916, 468.

*Silicates; Manufacture of soluble —.* J. W. Spensley and J. W. Battersby. Fr. Pat. 478,508, Apr. 24, 1915.

SEE Eng. Pat. 11,959 of 1914; this J., 1915, 834.

*Aluminium nitride; Process and apparatus for manufacture of —.* Soc. Gén. des Nitrures. Fr. Pat. 478,886, Aug. 14, 1914.

SEE Eng. Pat. 11,271 of 1915; this J., 1916, 115.

*Nitrogen; Process of fixation of —.* A. Badin, Assignor to Soc. Gén. des Nitrures, Paris. U.S. Pat. 1,196,639, Aug. 29, 1916. Date of appl., Nov. 18, 1914.

SEE Eng. Pat. 22,586 of 1914; this J., 1915, 353.

*Nitrogen; Process for the fixation of — by means of ferro-aluminium.* P. Bunel, Assignor to Soc. Gén. des Nitrures, Paris. U.S. Pat. 1,196,657, Aug. 29, 1916. Date of appl., Apr. 3, 1915.

SEE Eng. Pat. 4287 of 1915; this J., 1915, 961.

*Carbon monoxide from carbon and oxygen; Preparation of —.* Soc. pour l'Ind. Chim. à Bâle. Fr. Pat. 478,166, July 22, 1914.

SEE Ger. Pat. 280,968 of 1913; this J., 1915, 613.

*Hydrogen and lampblack; Process for making —.* American Nitro Products Co. Fr. Pat. 478,212, Mar. 31, 1915.

SEE U.S. Pat. 1,168,931 of 1916; this J., 1916, 309.

*Carbon dioxide and nitrogen; Production of — by combustion of carbonaceous substances.* American Nitro Products Co. Fr. Pat. 478,213, Mar. 31, 1915.

SEE U.S. Pat. 1,151,172 of 1915; this J., 1915, 1114.

## VIII.—GLASS; CERAMICS.

### PATENTS.

*Firebrick chequer work used in regenerative chambers and the like.* Gibbons Bros., Ltd., Lower Gornal, and F. W. Clark, London. Eng. Pat. 11,911, Aug. 18, 1915.

*[Glass] furnaces; Recuperative —.* Empire Machine Co. Fr. Pat. 479,289, July 16, 1915.

SEE Eng. Pat. 10,157 of 1915; this J., 1916, 549.

*Glass; Manufacture of —.* R. G. Kann. Fr. Pat. 479,370, July 24, 1915.

SEE Eng. Pat. 10,446 of 1915; this J., 1916, 541.

## IX.—BUILDING MATERIALS.

*Portland cement; Properties of the calcium silicates and calcium aluminates occurring in —.* P. H. Bates and A. A. Klein. U.S. Bureau of Standards, Technologic Paper 78. J. Franklin Inst., 1916, 182, 398—401.

To obtain  $3\text{CaO}.\text{SiO}_2$  and  $2\text{CaO}.\text{SiO}_2$ , the corresponding mixtures of lime and silica were heated in the presence of small amounts of boric acid or chromic oxide; six successive burnings were

required to obtain the tricalcium compound. Tricalcium aluminate is not stable at its melting point; it was produced by heating for some time below this point without the use of any catalyst. The aluminate sets and hydrates so rapidly and with so much evolution of heat that it is almost impossible to make test pieces. It never attains a greater tensile strength than 100 lb. per sq. in. When mixed with the silicate it reduces the time of setting and slightly reduces the strength of the silicate. Dicalcium silicate sets so slowly that it is difficult to obtain satisfactory test-pieces. After 1 year it has a tensile strength of 600 lb. per sq. in. at 5.5% water of hydration. After 14 days test-pieces break at 60 lb. per sq. in. Even after 1 year the mass is sandy, granular, and porous. Its strength is slightly increased by mixing with 3% plaster or with 19 parts of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . When mixed with equal parts of  $3\text{CaO} \cdot \text{SiO}_2$ , it reduces the early strength of the latter, but later gives a good cement. The tricalcium silicate has properties resembling those of Portland cement. At the end of a week the mass is very dense with a semi-vitreous lustre. It is not adapted to withstand moisture or changes of temperature. The addition of aluminate to it reduces the early strength; plaster and aluminate increase the early strength but reduce the later strength. Addition of the disilicate reduces the early strength, but the strength increases constantly with age. The addition of aluminate to the mixture of the two silicates increases the early strength, but is of no advantage later. The preponderance of either silicate in a cement is undesirable.—A. R. S.

*Plaster of Paris; Influence of various substances on the setting of—*. E. Canals. J. Pharm. Chim., 1916, 14, 33–37, 78–83. (See also this J., 1916, 470.)

The sulphates, chlorides, nitrates, bromides, and iodides of potassium, sodium, and ammonium, sodium and potassium hydroxides, sulphuric, hydrochloric, and nitric acids, the sulphates of zinc, iron, and copper, sodium phosphate, potassium carbonate, calcium oxide, and soap accelerate the rate of setting of plaster of Paris, whilst boric acid, borax, sodium and potassium silicates, sodium, calcium, and magnesium carbonates, sugar, glycerin, and alcohol have a retarding action, and manganese dioxide, copper oxide, barium hydroxide, ammonia, silica, and barium sulphide have little or no influence. In general, substances which increase the solubility of plaster of Paris accelerate the rate of setting, whilst conversely those substances such as borax, sodium carbonate, sugar, alcohol, and mucilaginous substances, which diminish the solubility, retard the rate of setting. In the case of salts which accelerate the rate of setting of plaster of Paris, the stronger the acid or base the greater is the acceleration.—T. C.

#### PATENTS.

*Stone; Treated—*. R. W. Hyde. Lakewood, Ohio. U.S. Pat. 1,196,693, Aug. 29, 1916. Date of appl., Dec. 18, 1914.

SANDSTONE is hardened, toughened, and rendered non-absorbent and non-conducting for electrical purposes by filling the interstices with linseed or other vegetable oil.—A. B. S.

*Impermeable [building] materials; Manufacture of—*. L. S. Van Westrum. Fr. Pat. 478,360, Apr. 12, 1915.

SEE Eng. Pat. 6823 of 1915; this J., 1916, 691.

*Building materials; Manufacture of—*. J. J. W. H. Van der Toorn. Fr. Pat. 479,720, Sept. 11, 1915.

SEE Eng. Pat. 13,081 of 1915; this J., 1916, 424.

*Portland cement; Manufacture of—*. J. F. Goddard. Fr. Pat. 478,585, May 4, 1915.

SEE Eng. Pat. 13,542 of 1914; this J., 1915, 426.

*Cement; Manufacture of slow-setting hydraulic —, containing little or no alumina*. J. Gresly. Fr. Pat. 478,936, June 7, 1915.

SEE Eng. Pat. 8551 of 1915; this J., 1916, 180.

*Shaft-furnace for burning cement, lime, and similar substances*. Steiger-Krauer und Co., and O. Frey. Fr. Pat. 479,292, July 16, 1915.

SEE Eng. Pat. 10,338 of 1915; this J., 1916, 891.

*Cement-asbestos tiles and the like; Manufacture of—*. R. E. Golightly. Fr. Pat. 479,321, July 20, 1915.

SEE Eng. Pat. 18,005 of 1914; this J., 1915, 835.

*Slag; Treatment of— for the manufacture of bricks, etc.* E. R. Sutcliffe. Fr. Pat. 479,332, Aug. 19, 1914.

SEE Eng. Pat. 18,806 of 1913; this J., 1914, 964.

*Fibrous compositions. [Roofing sheets.]* Eng. Pat. 8815. See V.

## X.—METALS; METALLURGY, INCLUDING ELECTRO-METALLURGY.

### Mineral survey of the British Empire.

A MEMORANDUM has been submitted to the Government by the Iron and Steel Institute, Institute of Metals, Institution of Mining Engineers, and Institution of Mining and Metallurgy, pointing out the necessity of forming a central Imperial Department of Minerals and Metals, the object of which would be to protect and advance the economic welfare of the mineral and metal industries of the Empire. It is pointed out that several of the home Government departments have been concerned with collecting information on sources of supply of minerals and metals, but that there has been much overlapping and duplication of effort, since no serious attempt has been made to co-ordinate and render available the information so collected. The proposed Department of Minerals and Metals should be in intimate relationship with the Geological Surveys and Mines Departments of the Dominions, and also with the organisations representing the different branches of the mining and metallurgical industries. The Geological Survey of Great Britain and Ireland and the Museum of Practical Geology should also form an integral part of the Department. The duties of a Department of Minerals and Metals would include:—

1. Arrangements for expediting the completion of mineral surveys of the United Kingdom and of the Crown Colonies and other British possessions.

2. The systematic collection and co-ordination of information bearing on the occurrence, uses, and economic value of minerals and their products, special attention being devoted to securing industrial applications for newly-discovered minerals or metallurgical products, and to finding mineral materials required for new metallurgical products or inventions. Some of this information should be promptly and widely disseminated in summarised form to those interested in the industries, through the medium of the existing publications of the institutions directly concerned.

3. The investigation of all questions and problems relating to the utilisation of the mineral or metallurgical resources of the Empire.

4. The co-ordination and dissemination of information on mining laws, development of mineral areas, output, processes of extraction, plant, capital employed, markets, etc.

5. A general review from time to time of the developed and undeveloped mineral resources, and of the position of each mineral or metal, to ensure that the mineral wealth of the Empire is being exploited with due regard to Imperial interests.

6. Generally, to advise the Imperial Government on all questions bearing on the mining and metallurgical industries. To perform this function efficiently, it is essential that complete information should be available, and also that the industries concerned should be consulted through their respective organisations.

*Wrought iron; Effect of blast-furnace gases on —.* J. E. Stead. Iron and Steel Inst., Sept., 1916. [Advance proof.] 7 pages.

AFTER exposure to hot blast-furnace gases for a year, closed wrought iron tubes (containing test-bars of polished steel) were found to be blistered and superficially disrupted in places and to have carbon deposited within and upon them; a slight deposition of carbon upon the polished test-bars was also observed. As the result of investigation it is concluded that, at 400°—500° C., carbon monoxide is decomposed by the external scale and enclosed magnetic cinder of wrought iron, carbon being deposited; that wrought iron containing free oxides is liable to disruption from this cause; and that, under the conditions named, even initially unoxidised steel acts upon carbon monoxide and induces carbon to be deposited on its surface.—W. E. F. P.

*[Steel] ingots; Some properties of —.* A. W. and H. Brearley. Iron and Steel Inst., Sept., 1916. [Advance proof.] 34 pages.

THE effects of crystal growth, crystalline structure, shrinkage, and variations in casting temperature, shape of mould, etc., on the properties of steel ingots were studied by direct examination of the latter and by analogy from the behaviour of molten stearine cast under various conditions. By this means the common defects and peculiarities of steel ingots were found capable of simple explanation and to be often preventable. For the production of sound steel ingots, bottom casting is regarded as advantageous mainly because the shrinkage cavities are more likely to be clean and therefore capable of being welded up. Segregation and the occurrence of ghost lines in large ingots are also considered and explained by reference to the behaviour of molten stearine on cooling. The use of stearine for studying the properties of ingots is strongly advocated, the higher coefficient of shrinkage, lower resistance to tensile stresses, and lower heat conductivity of this material as compared with steel being considered advantageous, since the defects found in the ingots, although similar to those likely to occur in steel, are generally exaggerated and therefore more clearly visible.—W. E. F. P.

*Carbon steels; Influence of heat treatment on the thermo-electric properties and specific resistance of —.* E. D. Campbell. Iron and Steel Inst., Sept., 1916. [Advance proof.] 18 pages.

MEASUREMENTS of specific resistance and thermo-electromotive force were made on similar specimens of nine different carbon steels which had been quenched from 908° or 903° C. and reheated to temperatures increasing by approximately 100° from 100° to 800° C.; the steels contained up to 1.05% C, 0.221% Mn, 0.016% P, 0.041% S, and 0.169% Si, and in one case 0.018% Cu. From the parallelism found between the two sets of results, it is concluded that, like the total specific resistance,

the total thermo-electromotive potential of steel is made up of two components, due to the solvent iron and the solutes, respectively; the proportion due to the latter depends upon the extent to which they are in solution. This parallelism is regarded as strong confirmatory evidence of the essential unity of mechanism existing between metallic and aqueous solutions. The transformation of the allotropic into the  $\alpha$ -form of iron was found to be nearly completed after reheating to 300° C.; but complete equilibrium, as indicated by minimum specific resistance and thermo-electromotive force, was only attained after long heating at about 700° C. Neither the specific resistance nor the thermo-electromotive force due to carbon in solution as carbides was found to be directly proportional to the atomic concentration of the carbon, the effects produced by equiatomic concentrations of carbon as hypoeutectoid carbides and eutectoid or hyper-eutectoid carbides being as 1:2 approximately. From the results of the investigation it is also concluded that constancy of thermo-electromotive force in couples can only be obtained when the molecular concentration of those members not consisting of strictly pure metals remains constant over the required temperature range; since the thermo-electromotive force is independent of the size and shape of the cross-section between the points of contact but wholly dependent on the molecular composition and the temperature gradient between these points, it should not be difficult to devise a method for detecting the molecular changes which may have been induced in a given piece of steel by heat treatment.

—W. E. F. P.

*Nickel-steel scale, and the reduction of solid nickel and copper oxides by solid iron.* J. E. Stead. Iron and Steel Inst., Sept., 1916. [Advance proof.] 6 pages.

CHEMICAL and micrographical examination of a nickel-steel (25% Ni) ignition tube, after prolonged use in a gas engine at temperatures approximating 800°—1000° C., showed that the iron had been selectively oxidised and the nickel concentrated in the outer part of the metal by interdiffusion of nickel and iron and removal of the latter as oxide at the surface. Oxidation had proceeded along the crystal junctions of the metal, the grains of which had become gradually diminished in size, enriched in nickel, and enveloped in oxide scale, until they finally appeared as independent inclusions in the latter. The adherence of the scale to the alloy (and nickel steels generally) was found to be due to interpenetration of the metals and oxides. Further investigation showed that, at temperatures much below the melting point of either material, nickel and copper oxides were reduced to the respective metals by iron, with formation of iron oxide. This interchange was not confined to the surfaces of contact, but extended for a considerable distance below the surface of the iron, showing that interdiffusion had occurred between iron and nickel, iron and copper, and the corresponding oxides.—W. E. F. P.

*Nickel (in iron and steel); Use of diphenylglyoxime as indicator in the volumetric determination of — by Frevert's method.* G. L. Kelley and J. B. Conant. J. Ind. Eng. Chem., 1916, 8, 804—807.

FREVERT'S volumetric method for the determination of nickel in iron and steel (Blair, "Chem. Anal. of Iron," 7th ed., 1912), modified as described below, has been found to give results nearly as accurate as the gravimetric determination with dimethylglyoxime. The sample (1 grm. for a nickel content between 0.1 and 5%) is dissolved in 50 c.c. of hot nitric acid of sp.gr. 1.13 or in 60 c.c. of hydrochloric acid (1:1); iron and carbides are oxidised by adding nitric acid, drop

by drop, to the solution until effervescence ceases. After boiling to expel nitrous fumes, and cooling, the solution is treated successively with 12 grms. of citric acid, 20 c.c. of ammonia solution of sp.gr. 0.9, sufficient dimethylglyoxime solution (20 grms. dissolved in 1300 c.c. of ammonia of sp.gr. 0.9 and made up to 2000 c.c.) to precipitate the nickel, and a slight excess of ammonia. The precipitate, after standing for 1 hour if the quantity of nickel is small, is collected on asbestos, washed with water, and dissolved on the filter in nitric acid. The solution and washings are treated, whilst nearly at the boiling point, with 1 gm. of potassium chlorate or ammonium persulphate, and boiled until clear. Alternatively the precipitate may be dissolved in a mixture of 40 c.c. of hydrochloric and 10 c.c. of nitric acid, and the solution boiled until clear. The clear solution is cooled, made slightly ammoniacal, using rosolic acid as indicator, and is then treated with 10 c.c. of potassium iodide solution (8 grms. per litre) and 10 c.c. of silver nitrate solution (0.5 gm. per litre), and titrated with potassium cyanide solution (1 c.c. = 0.001 gm. Ni) until the last trace of opalescence disappears. A blank test is made by titrating with potassium cyanide a nickel solution which has already been titrated and to which 10 c.c. each of the potassium iodide and silver nitrate solutions have been added subsequently; the volume of the solution to be titrated should always be about 250 c.c.

By using diphenylglyoxime (Atack, this J., 1913, 789) as indicator, the end point of the titration may be recognised by a colour change. The dimethylglyoxime precipitate (see above) is dissolved in concentrated hydrochloric acid containing 10% of nitric acid, the solution and washings are evaporated nearly to dryness, diluted to 150–200 c.c., and rendered alkaline by adding 5 c.c. of dilute (1:3) ammonia. Excess of standard potassium cyanide solution is then added and the excess titrated with a standard solution of nickel sulphate, using 5 c.c. of diphenylglyoxime solution (1 gm. dissolved in a solution of 5 grms. of sodium hydroxide in 100 c.c. of water, and the solution diluted to 1 litre) as indicator.—A. S.

**Gold and copper ores, Mount Morgan, Queensland; Flotation of—** W. Shellshear. Proc. Australasian Inst. Min. Eng., 1916, 51–74.

THAT portion of the ore too silicious for economical smelting, containing approximately Cu 2, Fe 10, SiO<sub>2</sub> 73, Al<sub>2</sub>O<sub>3</sub> 1.5, CaCO<sub>3</sub>, etc. 3.5%, and Au 5.5 dwt. per ton (or about 6% of iron pyrites, 16 of copper pyrites, and 78 of quartz, calcite, etc.) was dry crushed to pass a 50-mesh screen and then subjected to flotation in a laboratory apparatus and in a 6-box standard 24-inch Minerals Separation machine, the latter being subsequently incorporated in an experimental plant having a capacity of 100 tons per day. In a typical experiment with the large machine, the rate of feed was 15 tons per hr.; dilution of pulp, 3.5 to 1; oil (eucalyptus), 1 lb. per ton; and duration of run, 3 hrs.; the recoveries of gold, copper, and iron were 69.8, 84.2 and 48.7% by weight, respectively. Owing to the low recovery of gold as compared with that of copper, various large and small-scale concentration tests were made on the ore on Wilfley tables and with Sonstadt's solution (mercuric iodide in aqueous potassium iodide), before and after flotation. The results indicated that the gold, although mainly associated with the copper, was really "free" but very finely divided and therefore only fully released by fine grinding. This was confirmed by the results of further direct flotation tests in which recoveries of 80% of the gold and 96.3% of the copper were obtained on the 120-mesh, as against 70% and 86% respectively on the 50-mesh ore. In all cases flotation was

effected in a neutral medium, acid not being employed with ores of this class. As flotative agents, eucalyptus oils alone or in admixture with other oils were used; and of the former, those containing phellandrene (viz., *Eucalyptus amygdalina* and *E. dives*) gave the best results. Various mixtures of good eucalyptus with "residuum" oils were also employed, with highly satisfactory results as regards both extraction and oil cost. Further tests were made in which both non-smelting and smelting ores were concentrated by vanning and the tailing treated by flotation; and in most cases the recovery of gold was appreciably greater than that obtained by direct flotation. Consequently, the treatment finally adopted for the non-smelting ore consisted in crushing to about 40-mesh size, concentrating by means of tables, re-crushing the "table rejects" to 80 or 120-mesh size and treating the latter by flotation. The following are details of results obtained and costs incurred over a period of one month, during which the non-smelting ore was treated by direct flotation in the experimental plant:—Crude ore milled, 83 tons per day; average rate of rock-breaker, 12 tons per hr.; average rate of ball mills, 0.98 ton per hr. per mill; average feed to flotation plant, 17.3 tons per hr.; assay of crude ore, Cu 2.10%, Au 6.01 dwt. per ton; actual recoveries, 68.58% of the gold and 80.00% of the copper; total cost of treatment, 5s. 4.09d. per ton, including 1s. 5.18d. for flotation of which 4.08d. represented the cost of oil.—W. E. F. P.

**Silver; Allotropy of—** W. D. Helderman. Inst. of Metals, Sept., 1916. [Advance proof.] 24 pages.

FROM pycnometric and dilatometric observations made on silver obtained by various methods and after different treatments, it is concluded that pure silver consists of at least three allotropic (enantiotropic) forms, and has a transition point at about 77° C.; that all objects made of silver are in a metastable condition owing to retardation of the transition of the altered form; and that all the present physical constants of silver, except the atomic weight, refer to indefinite mixtures of the different allotropic forms.—W. E. F. P.

**[Copper] leaching plant; A 2000-ton — at Anaconda, Mont.** F. Laist and H. W. Aldrich. Min. and Eng. World, 1916, 8, 321–325.

THE plant, completed in May 1915, works up tailings from a dump of about 20,000,000 tons, averaging Cu 0.64% and Ag 0.48 oz. per ton. The material is conveyed to wooden storage bins holding 6000 tons, thence by belts to 28 roasting furnaces of the McDougall six-hearth type. The furnaces are air-cooled, the heated air being used in the leaching plant for warming the liquors. The tailings are subjected to a simple oxidising roast at about 535° C., and the calcinate passes through a cylindrical cooler, the dust being settled by adding about 1% of water. The leaching plant consists of 10 redwood tanks of a capacity of 1000 tons of calcinate each. The leaching is done by continuous downward percolation through cocoa matting covered by a grating. The charge is treated successively with (1) 250 tons of liquor containing 5% of sulphuric acid and 7% of salt; (2) 100 tons of solution containing 20% of acid, and salt equal to 1% of the weight of calcine; (3) 150 tons of solution containing 0.5% of acid and 3.5% of salt; (4) 300 tons of hot water. The iron oxide in the calcinate yields ferric chloride which dissolves much unaltered sulphide, while the strong brine leaches out the silver. The spent liquors, after removal of the copper, are used over again except one-third of the first liquor, which is discarded so as to prevent accumulation of iron and aluminium sulphates. The precipitation of copper and silver

is accomplished by scrap iron resting on heavy wood gratings in concrete launders, 250 ft. long and 4 by 8 ft. in section. The salt in the solution prevents the copper from plating the iron, and gives a soft spongy cement copper which is easily washed off with a hose. The precipitate, containing 70% of copper, is deposited in settling-tanks, washed, and briquetted for blast-furnace treatment. The extraction averages 80% of the copper and 80% of the silver.—W. R. S.

*Copper: Occurrence and significance of twinned crystals in electrolytic*—H. S. Rawdon. U.S. Bureau of Standards. Amer. Inst. Metals, Sept., 1916. [Advance proof.] 12 pages.

From a study of deposits of electrolytic copper obtained at various current densities, it is concluded that the variation in crystal size alone is not sufficient to account for the observed differences in physical properties. Except when obtained at low current densities, the deposits have similar properties to those of metals hardened by cold working, and the existence of this condition is confirmed by the behaviour on annealing. These conclusions are regarded as applicable to all electro-deposited metals.—W. E. F. P.

*Tinned sheet copper; A case of corrosion of*—P. D. Merica. Amer. Inst. of Metals, Sept., 1916. [Advance proof.] 10 pages.

The upper side of tinned sheet copper that had been in use for 22 years as roofing material showed numerous small pits  $1/32$ — $1/64$  in. in diameter, and furrows of the same width with a length of up to 2 in. The pits were distributed along lines of surface scratches, the scratch passing through the centre of each pit. Micrographs showed the tin coating to be composed of three layers, the one next to the copper, 0.002 mm. thick, being identified as Cu<sub>2</sub>Sn. This has been shown to be electro-negative to copper, tin, and their eutectic. It is concluded that the corrosion is due to galvanic action between the constituents of the layers; its local character is explained by scratches and mechanical injuries.—W. R. S.

*Spelter; Cadmium in*—W. R. Ingalls. Inst. of Metals, Sept., 1916. [Advance proof.] 3 pages.

SLABS of spelter as supplied by the smelter are not of exactly uniform composition, as the kettle into which the metal is received from the furnace holds a relatively small quantity, and the impurities passing over with the zinc vary in amount in different parts of the furnace, according to the temperature of the retort. To ensure uniformity the zinc should be remelted in large pots or furnaces before being cast into slabs for delivery. Spelter free from cadmium can only be obtained by single smelting when the ore is free from cadmium, but by redistilling common spelter with proper control of the temperature, and separating the first distillate, a high-grade spelter, low in cadmium, is easily produced. It is stated that excessive prices have recently been paid for American high-grade spelter, which is merely redistilled common spelter. Zinc free from cadmium is easily obtained electrolytically, but the electrolytic process is commercially applicable only under limited favourable conditions. Cadmium is deleterious in zinc to be used for slush castings, and is objectionable in cartridge brass, but for brass that is to be cast and machined, the adverse effect of cadmium is probably overestimated, and may be non-existent. T. St.

*Manganese bronze; Initial stress produced by the burning-in of*—P. D. Merica and C. P. Karr. U.S. Bureau of Standards. Amer. Inst. Metals, Sept., 1916. [Advance proof.] 8 pages.

From an investigation of the causes of failure of

large valve castings of manganese bronze, which had been treated or repaired by welding or burning-in, it is concluded that unless the shape of the casting is such as to permit extensive distortion, local initial tensional stresses—equal in value to the true elastic limit of the material—are set up within or near the burnt-in zone. These stresses may be eliminated, and danger from subsequent cracking prevented, by heating the whole casting before welding so that all parts of the finished product cool down together from a dull red heat, or by annealing the finished casting at 400°—500° C. for 2 hours.—W. E. F. P.

*Alloys to withstand internal air pressure.* S. D. Sleeth. Amer. Inst. of Metals, Sept., 1916. [Advance proof.] 3 pages.

DENSITY and strength are the indispensable qualities of alloys (chiefly brass and bronze) used in the manufacture of articles intended for the retention of gases under pressure. The variable factors which influence these qualities, viz., design of article to be cast, design of pattern with reference to its position in the flask, composition of the alloy, treatment of the metal in the furnace, and temperature of pouring, are briefly discussed. The presence of aluminium in the alloys is especially injurious.—W. R. S.

*Lead; Volumetric determination of*—J. Waddell. Analyst, 1916, 41, 270—272.

ABOUT 1 gm. of the ore is digested with 10 c.c. of hydrochloric acid, and then evaporated with 5 c.c. of nitric acid till the volume is reduced to about 7 c.c. An excess of ammonia is added, then sufficient acetic acid to prevent precipitation of basic ferric acetate at a temperature near the boiling-point. The solution, measuring about 25 c.c., is treated with 10 c.c. of 10% potassium chromate solution; the precipitate may be filtered off after 5 minutes. After the excess of precipitant has been washed out with boiling water, the lead chromate is dissolved on the filter with 100 c.c. of hydrochloric acid (1:3) and the filtrate received in the original flask. It is best, though not indispensable, to dissolve most of the lead chloride formed on the filter by alternate washings with acid and water. The cold filtrate is made up to 200 c.c., treated with 1 gm. of potassium iodide, and titrated with sodium thiosulphate solution (18 grms. per litre) at the rate of 2—3 drops per second; the thiosulphate is standardised against lead or lead sulphate; a little starch solution is added towards the end of the titration. When the blue colour has almost disappeared, 10 c.c. of strong hydrochloric acid is added, the solution heated to about 40° C., and the titration finished. If the ore contains antimony, bismuth, silver, or decomposable silicates, the lead is first separated as sulphate, which is dissolved in ammonium acetate.—W. R. S.

*Radio-lead from pure Norwegian cleveite; Density of*—T. W. Richards and C. Wadsworth. J. Amer. Chem. Soc., 1916, 38, 1658—1660.

RADIO-LEAD prepared from purified lead sulphide from Norwegian cleveite, was found to have a density, 11.273, distinctly lower than that of Australian radio-lead (11.289; see this J., 1916, 363), and much lower than that of ordinary lead (11.337). The atomic weight of the radio-lead from Norwegian cleveite was 206.085.—A. S.

*Flotative agents [for ore concentration]; A source of*—[Wood tar from sage brush.] G. H. Clevenger. Bull. Amer. Inst. Min. Eng., Sept., 1916. Eng. and Min. J., 1916, 102, 420—424.

In seeking a convenient source of flotative agents for use in the arid mining regions of the Western States (U.S.A.), the native sage brush (*Artemisia*

*tridentata*) was destructively distilled and the products—acid liquor, alkaline liquor, and tar oil—tested qualitatively in conjunction with finely-ground galena, cinnabar, pyrites, and other minerals. The acid liquor behaved like ordinary pyroligneous acid; the alkaline liquor was a good frothing agent, but the froth carried up little mineral; the tar oil proved a very efficient floatative agent. In quantitative tests with the latter on zinc, lead, mercury, and silver-gold ores were generally better, and the oil consumption less, than with the majority of oils previously tried. The sage brush (30 lb. lot) yielded 3.96% of tar oil, 3.66% being with the acid liquor and 0.30% with the alkaline liquor; probably 4% would be an average yield if the plant were collected at the proper season and the distillation efficiently conducted. By steam distilling the tip ends of the shrub, a quantity of essential oil corresponding to 0.43% of the whole plant was obtained; but for floatation purposes this product was much less efficient than the tar oil.—W. E. F. P.

**Ferro-tungsten and tungsten powder; Prices of —.**  
Board of Trade J., Sept. 21, 1916.

THE Ministry of Munitions announces that the price of ferro-tungsten is officially fixed at 5s. 6d. per lb. of tungsten content, and of tungsten powder at 8s. 3d. per lb., based on ore at 60s. per unit. The price of the product is on a sliding scale which rises or falls 1d. per lb. with each variation of 1s. per unit of ore.

**Japanese mines output in 1915.** Eng. and Min. J., Sept. 16, 1916.

The production of Japanese mines in 1915 was valued at £17,595,000, a gain of about 13.5% over the production of 1914. This figure does not include the production of the Government Iron Works, known to be greatly increased, through co-operation with the Russian Government in supplying war munitions. The amounts of the various products are shown in the following table:—

	Amount.	Percentage increase over 1914.
Gold, kg.	8,213	16.2
Alluvial gold, kg.	80	—
Silver, kg.	159,261	5.5
Copper, m. tons.	75,415	7.0
Lead, m. tons.	4,764	4.4
Bismuth, kg.	1,074	—
Bismuth ore, m. tons.	21	—
Tin, m. tons.	341	253.3
Antimony, refined, m. tons.	8,320	116.0
Antimony, crude, m. tons.	27	—
Mercury, kg.	38	—
Zinc, metal, m. tons.	21,131	274.0
Zinc ore, m. tons.	6,121	—56.9
Pig iron, m. tons.	64,897	—13.2
Wrought iron, m. tons.	1,168	69.0
Steel (except government works), m. tons.	16,741	8.9
Pyrites, m. tons.	67,536	—41.7
Chromite, m. tons.	2,979	41.3
Manganese, m. tons.	25,870	51.5
Scheelite, m. tons.	352	90.9
Wulfenite, m. tons.	11	—
Wulfenite, crude, m. tons.	10	—
Arsenic, kg.	14,885	—
Phosphate, m. tons.	57,723	50.9
Graphite, m. tons.	866	16.0
Coal, m. tons.	20,490,702	—8.1
Oil, litres.	470,390,580	10.8
Asphalt, m. tons.	1,975	—1.5
Sulphur, m. tons.	61,405	2.6
Sulphur, ore, m. tons.	17,174	—

**Iron and steel production of Canada.** Board of Trade J., Sept. 7, 1916.

THE production of iron and steel of various kinds in Canada during 1913, 1914, and 1915 was as follows:—

	1913.	1914.	1915.
Pig iron .....	Tons.* 1,015,118	Tons. 705,972	Tons. 825,420
Steel ingots and castings .....	1,042,508	743,352	912,755
Finished rolled iron and steel .....	967,097	659,519	653,318
Cut nails and wire nails .....	Kgs.† 1,520,000	Kgs. 1,144,000	Kgs. 1,636,000

\* 2240 lb.

† 109 lb.

The production of pig iron in Canada during the first six months of 1916 amounted to 507,750 long tons.

**Metals, ores, etc.; Trading in —.** Board of Trade J., Sept. 21, 1916.

THE Ministry of Munitions has announced that Defence of the Realm Regulation 30A applies to the following war material:—Aluminium and its alloys, unwrought and partly wrought, including ingots, notched bars, slabs, billets, bars, rods, tubes, wires, strand, cable, plates, sheets, circles, and strips. Granulated aluminium, aluminium powder, "bronze," "flake," and "fitter." Platinum metal and ores, residues, and bars containing the same.

Under Defence of the Realm Regulation 30B, except under certain conditions, it is not lawful for any person on his own behalf or on behalf of any other person to sell or buy, or to offer to sell or buy, (a) any of the following metals:—Iron (including pig-iron), steel of all kinds, copper, zinc, brass, lead, antimony, nickel, tungsten, molybdenum, ferro-alloys; or (b) any other metal which may be specified in an order of the Admiralty or Army Council or the Minister of Munitions as being a metal required for the production of any war material. Transactions will not be permitted, except under special licence, in scrap from high speed steel, scrap from copper, or scrap from brass. Transactions in other scrap metals do not require a licence.

Applications for licences in this connection should be addressed to the Director of Materials, Ministry of Munitions, Armament Buildings, Whitehall Place, London, S.W.

**Development of the spelter industry.** Smith. See page 996.

**Corrosion in a steel gasholder tank.** Wilson. See II.A.

**Fifty-second annual report on alkali, etc., works by the Chief Inspector.** 1915. See VII.

**Electro-analytical method for determination and separation of metals of the copper-tin group.** Schoch and others. See XXIII.

**Electro-analysis of silver with solutions of silver chloride in ammonia.** Schoch and Crawford. See XXIII.

**PATENTS.**

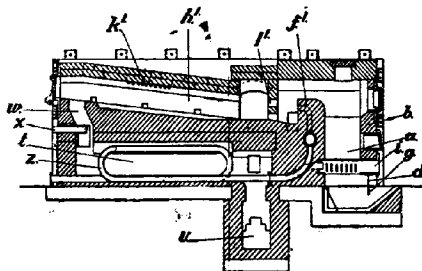
**Metal plates; Coating of — with tin, terne or other metal or alloy.** P. B. Taylor, Briton Ferry, S. Wales. Eng. Pat. 12,311, Aug. 26, 1915.

A SET of finishing rolls revolve in the flux, one or more of the lower rolls being of a different material from the top pair of tinning rolls. The lower rolls either do not take a coating of tin, or they permit the tin to drain from them more quickly than from the top rolls. The rolls on one side of the plates may be such as to produce a coating of different thickness from that on the other side. A cleaning, wiping, or distributing roll may be provided in contact with the tinning roll, with or without a trough for molten metal.—W. F. P.



*Furnaces; Heating*—[for metals]. R. F. Hislop. Paisley. Eng. Pat. 15,226, Oct. 28, 1915.

THE front wall, *b*, of the firebox, *a*, rests on a beam, *d*, spanning the ash-pan and having a plate, *g*, dipping into a water seal. An inverted V-shaped grate, *i*, is provided, and the products of com-



bustion pass over the bridge, *f'*, and through openings, *l'*, to the longitudinally divided combustion chambers, *k'*, which are provided with ribs, *k'*, to deflect the gases on to the material on the floor. The gases then pass by the passage, *w*, controlled by dampers, *x*, to three parallel flues, *t*, and thence to the chimney, *v*. The flues, *t*, contain coils, *z*, for heating the air supply to the grate, *i*, and to the bridge, *f'*, and also a coil for generating steam to be supplied to the grate.

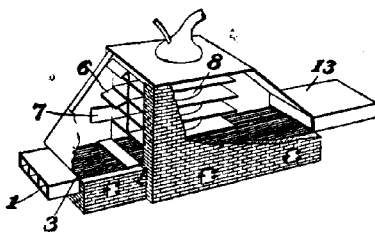
—W. F. F.

*Furnaces; Utilising waste heat from open-hearth* — R. M. Snyder, Wilkesburg, Pa. U.S. Pat. 1,195,521, Aug. 22, 1916. Date of appl., Dec. 27, 1915.

THE hot waste gases from two open-hearth furnaces are drawn by two similar fans through separate regenerators to two boilers. The supply of gases to the boilers is equalised by providing a cross connection between the two conduits.—W. F. F.

*Smelter or ore furnace; Apparatus for utilising the heated fumes from a* — G. P. Luedke, Chatham, Ill. U.S. Pat. 1,196,123, Aug. 29, 1916. Date of appl., Mar. 16, 1914.

A CASING is provided with a grate, 3, below which a flue, 1, with vertical partitions opens, and above which an exit flue, 13, is arranged. The upper part of the casing has inclined roof members, and



contains an arrangement of horizontal and vertical plates forming flues which can be controlled by dampers, 2, 6, 7. A vessel, 8, contains water which is heated by the fumes passing through the flues.—W. F. F.

*Metal ingots; Manufacture of* — Steel, Peech and Tozer, Ltd., and E. H. Saniter, Sheffield. Eng. Pat. 101,229, Jan. 12, 1916. (Appl. No. 497 of 1916.)

STEEL and other metal ingots are manufactured with little or no "pipe" by wholly or partly

covering the ingot when liquid with a plate of non-conducting material such as firebrick, or asbestos and cardboard, removing the covering just before solidification of the centre, and pouring additional liquid metal into the centre. To avoid any "pipe" from the added metal extending into the ingot, a head of brick or other non-conducting material is placed on the top of the ingot before filling the "pipe."—W. F. F.

*Tin ores; Process for removing iron from* — G. von Rauschenplat, Steglitz, Germany, Assignor to Barilla, Ltd., London. U.S. Pat. 1,196,043, Aug. 29, 1916. Date of appl., Jan. 28, 1914.

FERRUGINOUS tin ores containing tin oxide are subjected to a reducing treatment at a temperature below 500° C. and then treated with acid which dissolves the iron compounds but not the tin.

—W. F. F.

*Metal articles; Apparatus for disintegrating* — A. de Back, Essen, Germany, Assignor to Goldschmidt Detinning Co., New York. U.S. Pat. 1,196,343, Aug. 29, 1916. Date of appl., Dec. 29, 1914.

WASTE enamelled metal articles are passed between at least two pairs of rollers, the first pair having circumferential ribs and the second pair longitudinal ribs. The circumferential speed of the second pair is greater than that of the first pair so that a tension is exerted on the articles between the two pairs of rollers which corrugate the articles in two directions at right angles.—W. F. F.

*Blast-furnaces; Apparatus for detection of leakages in the water-jackets of* — L. S. Burt, London. From E. R. y Rizo, Portugalete, Spain. Eng. Pat. 101,327, May 31, 1916. (Appl. No. 7683 of 1916.)

*Cleaning metallic or like objects; Method and apparatus for* — A. Stöckli, Geneva, Switzerland. Eng. Pat. 101,313, Mar. 24, 1916. (Appl. No. 4390 of 1916.)

*Cementation process for armour-plates employing mixed cementation agents*. F. Giolitti, Turin. Assignor to Soc. Anon. Ital. Gio. Ansaldo & Co., Genoa, Italy. U.S. Pat. 1,195,459, Aug. 22, 1916. Date of appl., Oct. 14, 1914.

SEE Eng. Pat. 18,386 of 1914; this J., 1915, 88.

*Iron, steel, and the like from waste enamelled articles; Method of recovering* — A. de Back, Essen, Germany, Assignor to Goldschmidt Detinning Co., New York. U.S. Pat. 1,196,342, Aug. 29, 1916. Date of appl., Nov. 12, 1910.

SEE Fr. Pat. 418,971 of 1910; this J., 1911, 92.

*Steel; Treatment of* — C. H. A. F. L. Ross. Fr. Pat. 478,232, Apr. 1, 1915.

SEE U.S. Pat. 1,151,049 of 1915; this J., 1915, 1017.

*Steel; Treatment of* — C. P. Sandberg. Fr. Pat. 479,497, Aug. 10, 1915.

SEE Eng. Pat. 8257 of 1915; this J., 1916, 363.

*Iron and steel; Manufacture of — and melting of ores, metals, and other refractory materials*. F. G. C. Rincker. Fr. Pat. 479,168, June 29, 1915.

SEE Eng. Pat. 14,215 of 1915; this J., 1916, 969.

*Iron, steel, etc.; Superficial oxidation of articles of* — B. Guerini. Fr. Pat. 479,370, May 6, 1915.

SEE Eng. Pat. 7097 of 1915; this J., 1915, 1149.

*Rust; Electrolytic process for removing oxide or* — P. Marino, London. U.S. Pat. 1,195,704, Aug. 22, 1916. Date of appl., Apr. 25, 1916.

SEE Eng. Pat. 14,230 of 1915; this J., 1916, 849.

*Agglomerating finely-divided granular or friable materials [ores, flue-dust, etc.]; Process of*—  
A. V. M. Kroll, Luxemburg. U.S. Pat. 1,106,705,  
Aug. 29, 1916. Date of appl., Dec. 3, 1912.  
SEE Fr. Pat. 452,631 of 1912; this J., 1913, 757.

*Melting metals; Process and furnace for*—E.  
Bosshardt. Fr. Pat. 477,061, Mar. 8, 1915.  
SEE U.S. Pat. 1,164,983 of 1915; this J., 1916, 260.

*Metals; Electrolytic process for cleaning*—  
*Apparatus for electrolytic and analogous processes.*  
A. E. Battle. Fr. Pats. 479,004 and 479,005,  
June 11, 1915.

SEE Eng. Pat. 14,513 of 1914; this J., 1915, 910.

*Alloy.* C. R. Denton. Fr. Pat. 479,275, July 13, 1915.

SEE Eng. Pat. 17,157 of 1914; this J., 1915, 35.

*Sulphide ores; Roasting of*—Nichols Copper  
Co. Fr. Pat. 479,279, July 15, 1915.

SEE Eng. Pat. 9958 of 1915; this J., 1915, 1150.

*Tin; Electrolytic refining of*—American  
Smelting and Refining Co. Fr. Pat. 479,569,  
Aug. 20, 1915.

SEE U.S. Pat. 1,157,830 of 1915; this J., 1915, 1212.

*Zinc; Electrolytic recovery of*—from ores and  
other materials. U. C. Tainton. Fr. Pat.  
479,702, Aug. 16, 1915.

SEE Eng. Pat. 11,335 of 1915; this J., 1916, 969.

## XI.—ELECTRO-CHEMISTRY.

*Alkaline storage battery; The active materials and electrolyte of the*—L. C. Turnock. Met. and  
Chem. Eng. 1916, 15, 259–262.

NICKELOUS hydroxide is prepared by converting the metal into pure nickel sulphate, and then precipitating with caustic soda; pure metallic iron is prepared from Norwegian or Swedish iron by converting it into pure ferrous sulphate, roasting this to ferric oxide, and reducing with hydrogen liberated when dissolving the nickel and iron. The metallic iron is mixed with a small quantity of mercuric oxide. The electrolyte consists of a 21% solution of potassium hydroxide for a "first" electrolyte, and a 25% solution for "renewal" electrolyte, containing respectively 50 grms. and 15 grms. of lithium hydroxide per litre. These are produced respectively from potassium chloride electrolytically and from lithium carbonate by the action of lime. The method of testing the nickelous hydroxide and the iron for electrical capacity in miniature cells is described.—B. N.

*Light; A new way of converting*—into electrical energy. T. W. Case. New York Elec. Soc.,  
June 14, 1916. 12 pages.

EXPERIMENTS have been made with a cell containing plates of copper, oxidised in a flame, immersed in tapwater or a sodium chloride electrolyte, and a feeble current was produced on exposing the front plate to sunlight, the back plate being shielded and acting as the zinc of an ordinary battery. Similar results have been obtained with polished unoxidised copper plates, the one exposed to light turning gradually red, then purple and greyish-black, even though the plates were covered with several coats of white paint or bath enamel, and, though the action is somewhat weaker, exposed merely to diffused daylight. An E.M.F. of over 0.1 volt and a current of 0.2 ampère have been thus obtained from a cell containing two plates of copper, 6 in. square; the plate exposed

to light was oxidised in a flame and the other plate was polished.—B. N.

*Electrolytic preparation of chromous salts from chromic salts, and some new salts of divalent chromium.* Traube and Goodson. See VII.

*Electro-analytical method for determination and separation of metals of the copper-tin group.* Schoch and others. See XXIII.

*Electro-analysis of silver with solutions of silver chloride in ammonia.* Schoch and Crawford. See XXIII.

## PATENTS.

*Electric furnaces of the electrode type.* H. J. Kitchen, and T. Balmforth and Co., Luton. Eng. Pat. 101,201, Mar. 10, 1916. (Appl. No. 8533 of 1916.)

THE water jackets for cooling the electrodes, instead of being fixed to the roof, are each supported by arms fixed to a vertical rod carried by a bracket on the side of the furnace. The rod is adjustable vertically and is pivoted on the bracket, thus enabling the arms and water jacket to be swung clear of the roof.—B. V. S.

*Furnace; Electric arc*—for the treatment [reduction] of gases. C. O. A. Dövre, Notodden, Assignor to Norsk Hydroelektrisk Kvaelfstof-aktieselskab, Christiania, Norway. U.S. Pat. 1,194,606, Aug. 15, 1916. Date of appl., May 10, 1915.

GAS inlet openings are disposed at an angle in the side walls of the furnace to deliver gas over the area of a disc-like flame spread magnetically, and gas outlets are located between the centre and the periphery of the disc. Each outlet is surrounded by a number of inlet openings, and the outlets are provided with means for cooling the gases; with the object of obtaining short gas passages in the furnace and an effective cooling of the gases after leaving the furnace chamber.—B. N.

*Electrolytic cell.* H. T. Shriver, West Orange, N.J. U.S. Pat. 1,181,549, May 2, 1916. Date of appl., Apr. 3, 1915.

SEVERAL flat plates, forming the electrodes, are bound face to face to form a cell of the filter-press type, each of the plates being recessed centrally to form a cell between the faces. A diaphragm is arranged between each pair of plates to separate the gases formed on the faces of adjacent plates, the gases being led from the recessed portions to closed gas chambers above, through ducts in walls separating the chambers and recesses. The gases are conveyed from the gas chambers to horizontal ducts extending through non-recessed parts of the plates from face to face, so that the recessed portions may be completely filled with liquid to a level normally higher than the horizontal ducts, without fear of the electrolyte entering the gas ducts.—B. N.

*Electric furnaces.* J. L. Dixon. Fr. Pat. 479,444, Feb. 20, 1915.

SEE Eng. Pat. 4742 of 1914; this J., 1915, 233.

## XII.—FATS; OILS; WAXES.

*Chinese wood oil; Examination of*—F. Browne. Chem. News, 1916, 114, 123.

A SPECIMEN of oil expressed from genuine nuts from Wuchow had the following characters:—Sp.gr. at 15°C., 0.9415; iodine value, 187; saponif. value, 191; heat test, 12 mins.; refractive index at 20°C., 1.5206; at 15°C., 1.5226. Based

on these figures and on the examination of oils accepted by buyers as genuine and satisfactory, the following specification was drawn up for South China wood oil:—(1) The oil shall be pale in colour (according to season's production) and commercially free from fooms, dirt, and moisture. The total impurities shall not exceed 1%. Impurities, not obviously adulterations, up to 5% shall not justify rejection unless so arranged, but an allowance shall be made for such impurities in excess of 1%. (2) The refractive index shall not be less than 1.5204 at 15° C.; the temperature correction shall be -0.0004 for each 1° C. from 15° to 35° C. (3) The sp.gr. at 15° C. shall not be less than 0.9400. (4) The oil shall satisfy the requirements of one or other of the heat tests devised by Worstall (this J., 1912, 997), Bacon (this J., 1912, 782), Browne (this J., 1912, 731), duration of test not to exceed 13 mins., or Chapman (this J., 1913, 32). The method of sampling adopted by the Hongkong Government is to draw about 1 oz. from each cask, and to condemn for export any sample with a refractive index below the specification figure. The approved samples are united and the heat test and sp.gr. determined. The casks of oil passing these tests are sealed with official lead seals for shipment. For determining the sp.gr. at temperatures other than 15° C. a correction of 0.00064 is applied for each 1° C. In the heat test the following thermometric correction is made for the cool column— $T + 0.00016(T - t)N$ , where  $T$  represents the observed temperature,  $t$  the mean temperature of the emergent column, and  $N$  the number of scale degrees on the emergent column.—C. A. M.

*Chrysalis oil; Hardened* — M. Tsujimoto. J. Ind. Eng. Chem., 1916, 8, 802—804.

CHRYSLIS oil (see this J., 1908, 455) can be refined satisfactorily by heating it with 5–10% by vol. of sulphuric acid of sp.gr. 1.39, and then treating with Kambara earth (this J., 1913, 12; 1915, 840). The refined oil when hydrogenated with the aid of a nickel catalyst, yields a white fat suitable for soap making. The liquid acids of chrysalis oil when hydrogenated in presence of platinum black yield a product consisting mainly of stearic acid. The solid fatty acids of the raw oil when treated by fractional precipitation with magnesium acetate from alcoholic solution, yield palmitic acid and a higher acid or acids, or, more probably, an eutectic mixture of palmitic and stearic acids. According to Marcusson and Meyerheim, the inner iodine values (iodine values of liquid fatty acids) are higher than 100 in the case of hardened fish oils, whereas hardened terrestrial animal oils give lower values. Two samples of hardened chrysalis oil having iodine values of 35.8 and 45.5 respectively, gave inner iodine values of 87.6 and 103.2.—A. S.

*Calamary oil*. M. Tsujimoto. J. Ind. Eng. Chem., 1916, 8, 801.

CALAMARY oil is obtained from the internal organs, especially the livers, of various species of cuttle-fish, and is produced in considerable quantities in Japan as a by-product in the manufacture of "dried cuttle-fish" (Jap. *Surume*). A sample examined by the author was a brownish-red liquid, of disagreeable odour and taste, and having the following characters: sp.gr. at 15°/4° C., 0.9316; acid value, 3.88; saponif. value, 189.6; iodine value (Wijs), 177;  $n_D^{20} = 1.4806$ ; unsaponifiable matter, 1.14%; glycerol (extraction method), 10.24%; oxidised acids, 0.7%; m.pt. of mixed fatty acids, 35°–36° C.; polybromide of mixed fatty acids (70.9% Br), 57.5%. The oil solidified in a few hours when cooled by ice. Its drying power is similar to that of sardine oil. The oil cannot be refined satisfactorily by means of

Kambara earth, but the unpleasant odour is removed almost completely and the oil bleached to a pale yellow by mixing it with about 5% of a 20% solution of caustic soda, heating to 60–70° C., and filtering. The oil can be easily hydrogenated with a nickel catalyst, yielding a white, tallow-like fat of m.pt. 43°–44° C., and iodine value 49.—A. S.

*Water-melon seeds from the Sudan* [; Fatty oil from —]. Bull. Imp. Inst., 1916, 14, 100–102.

SEEDS of the water-melon, extensively cultivated in the Kordofan province, yielded 23.6% of a brownish-yellow oil calculated on the air-dry weight. The oil had the following characters: sp.gr. at 15° C., 0.9230; solidif. point of the fatty acids, 30.5° C.; acid value, 8.4; saponif. value, 191.4; iodine value, 117.1%; Hehner value, 95.1. The oil appears to be very similar to others derived from cucurbitaceous seeds but the yield is somewhat low. The residual cake contains a high proportion of fibre, 41.9%, and its food value is low: crude proteins, 18.3; starch, 26.9%. The oil would be suitable for soap making but the cake could not be largely used in fadders on account of the high proportion of fibre. Valuations of the seeds (Sept.—Oct., 1915) ranged from £5 10s. to £7 per ton.—J. F. B.

*Surface tension measurements of solutions of soap and of solutions of soap and various alkalis; Results of relative —. Chemistry of laundering.* H. G. Elledge and J. J. Isherwood. J. Ind. Eng. Chem., 1916, 8, 793–794.

EXPERIMENTS were made with soap solutions of 0.05, 0.1, 0.15, 0.2, and 0.25% concentration and solutions of sodium carbonate of 0.05, 0.1, 0.15, 0.2, and 0.25% concentration respectively, or equivalent solutions of trisodium phosphate, sodium hydroxide, or sodium bicarbonate. The measurements of surface tension were made by the drop method at 100° C., using kerosene as the medium in which the drops were formed. Solutions which gave the highest drop numbers showed also the greatest detergent action as measured by the power of carrying lampblack through filter paper. Within the field examined the detergent power of a soap solution was greater the greater the quantity of alkali added. Equivalent quantities of sodium carbonate and trisodium phosphate gave practically identical results. Sodium hydroxide increased the drop number to a greater extent than the carbonate. The results indicate that in regard to their effect on the detergent power of soap the alkali salts of weak acids are equally efficient, with the exception of sodium bicarbonate which, in cold solutions, has no influence on the drop number of soap solutions.—A. S.

#### PATENTS.

*Copra; Machine for drying* — D. N. McChesney, Manila, P.I. U.S. Pat. 1,196,128, Aug. 20, 1916. Date of appl., Apr. 10, 1914.

THE copra is dried on trays placed in a series of compartments, through which passes a pipe from a heater, whilst air is forced through a second pipe, which is fixed above the heating pipe and has openings, controlled by shutters, into each compartment.—C. A. M.

*Cotton and other oil seed or material; Heater or cooker for* — O. Sheppard, jun., Assignor to The Murray Co., Atlanta, Ga. U.S. Pat. 1,196,597, Aug. 29, 1916. Date of appl., Mar. 15, 1913.

THE material is fed from a hopper and feeding chamber into a series of superposed heating chambers with communicating outlets. Outside the hopper and compartments is a vertical shaft

on which are mounted rotary gates in vertical lineament. These co-operate with the hopper and compartments, so that regulated quantities of the material can be automatically delivered at timed intervals into the successive chambers.

—C. A. M.

*Hydrogenation of unsaturated oils or fats.* J. Dewar and A. Liebmann. Fr. Pat. 479,143, July 1, 1915.

SEE Eng. Pat. 15,664 of 1914; this J., 1915, 1102.

*Waste waters from oil factories; Utilization of —.* D. A. Hansen. Fr. Pat. 479,249, July 10, 1915.

SEE Eng. Pat. 17,915 of 1915; this J., 1916, 898.

*Soap; Product and process of manufacturing a product having the properties of —.* G. Petroff. Assignor to Aktions Co. "Kontakt," Petrograd. U.S. Pat. 1,196,274, Aug. 20, 1916. Date of appl., July 25, 1913.

SEE Eng. Pat. 452,054 of 1912; this J., 1913, 665.

*Washing compounds.* J. T. Freestone, and W. and F. Walker, Ltd. Fr. Pat. 478,717, Dec. 17, 1914.

SEE Eng. Pat. 19,229 of 1914; this J., 1915, 491.

*Grinding machine [for oil-cake, etc.].* Eng. Pat. 12,015. See I.

*Hydrogenated oil food product.* U.S. Pat. 1,187,999, See XIXA

### XIII.—PAINTS; PIGMENTS; VARNISHES; RESINS.

*Pigments and paints; Physical characteristics of —.* H. A. Gardner. J. Ind. Eng. Chem., 1916, 8, 794—797.

The opacity or hiding power of a pigment is greater the greater the degree of fineness (up to a certain limit; compare Ostwald, this J., 1916, 697), the higher the refractive index, and the smaller the amount of oil absorbed by the pigment. The refractive indices of some pigments, determined with the petrographic microscope, were as follows:—quartz silica, 1.55; barium sulphate, 1.6; zinc oxide, 1.94; white lead (basic carbonate and basic sulphate), 2.0; zinc sulphide, 2.2—2.37. White lead and zinc white thus have about the same refractive power, but in a workable paint the proportion of pigment to oil is 70:30 in the case of white lead and 50:50 in the case of zinc white, and hence the former has the greater hiding power. The refractive power of lithopone appears to be 1.9—2.0; it was not possible to increase the hiding power by increasing the proportion of zinc sulphide in the pigment. Microscopical examination of lithopone indicates that the particles of barium sulphate are coated with particles of zinc sulphide; a product prepared by mixing together barium sulphate and zinc sulphide in the same proportions as in lithopone has an inferior hiding power. The adhesive properties and cementing values of paint pigments apparently increase with approach to the colloidal condition. Experiments are described showing that when pigments, even the so-called inert pigments, such as barium sulphate and silica, are ground with linseed oil, some of the pigment forms a colloidal suspension in the oil. According to Ingalls, the purest carbon black obtainable by burning oil contains only 80—90% of carbon, the remainder consisting of adsorbed carbon monoxide and dioxide, hydrocarbons, nitrogen, oxygen, and water. When the pigment is ground in oil, the adsorbed gases appear to be displaced by the oil owing to preferential adsorption of the latter. Other cases

of preferential adsorption are the displacement of water from white lead pastes and of alcohol from zinc white and lithopone pastes by linseed oil. The "foots" present in linseed oil and in varnish appears to be present in the form of a colloidal suspension and would be better removed by centrifuging, preferably after addition of suitable mineral matter, than by settling (compare Ayres, this J., 1916, 676).—A. S.

*Coumarone resin and its uses.* C. Ellis and L. Rabinovitz. J. Ind. Eng. Chem., 1916, 8, 797—801. (See also this J., 1890, 275.)

SOLVENT naphtha (b.pt. 160°—180° C.) was stirred for several hours with 1% of sulphuric acid of 66° B. (sp.gr. 1.84); the temperature did not rise above 35° C. After washing and distilling with superheated steam, the residue formed a transparent brown resin of the consistence of molasses, which carbonised but did not become harder when heated with 10% of sulphuric acid of sp.gr. 1.84 at 220° C. Other polymerising agents tried instead of sulphuric acid gave unsatisfactory results, except silver oxide which gave a product harder than that obtained with sulphuric acid; part of the silver oxide was reduced to metal. When the soft resin was distilled at 29 in. vacuum, 57.5% distilled over up to 180° C. The distillate was a highly viscous liquid, iodine value 28.5. The residual resin softened at 38° C., and melted at 71° C.; its iodine value was 38—43.5 and its saponif. value did not exceed 0.2. Films prepared from a solution of the hard resin in benzol proved resistant to the alkaline aqueous extract of cement. A review of the journal and patent literature on coumarone and indene resins is given.—A. S.

*Storax; Researches on —. I. Identification of conifer resin acids (abietic and pimaric acids).* M. Henze. Ber., 1916, 49, 1622—1632.

THE composition of storax resin, the solid constituent of the balsam, had apparently been established, notably by Tschirch and van Itallie, according to whom the resin consists of a single storesinol, m.pt. 156°—161° C.,  $C_{14}H_{20}O_2$ , in combination with cinnamic acid. The author has arrived at very different results and recognises at least five, possibly six, distinct substances. The major portion of the resin consists of a mixture of two isomeric acids,  $C_{20}H_{30}O_2$ , which have been found to be completely identical with abietic and pimaric acids, the principal components of the conifer resins. This is the first record of the production of these acids by a non-coniferous tree (*Liquidambar orientalis* M.). For isolating the resin acids, the storax was dissolved in 70% alcohol on the water-bath and allowed to stand in the cold overnight. A heavy dark oil separated, apparently consisting of styracin; the alcoholic solution was treated with alcoholic lead acetate, the precipitate redissolved by heating, and allowed to crystallise out. The lead salt was separated, dried, and purified by recrystallisation, then dissolved in acetic acid and alcohol and poured into water. The resin acids, after recrystallisation, melted at 140°—150° C. and were finally separated, through their sodium salts and by recrystallisation from diluted methyl alcohol, into sparingly soluble pimaric acid, m.pt. 210°—211° C., in smaller quantity, and more soluble abietic acid, m.pt. 158°—165° C., in larger quantity. The filtrate from the lead precipitate yielded on saponification, besides cinnamic acid, a resinous mixture containing three or four bodies unidentified, one of which is ketonic and another alcoholic in function, also a resene body of high melting point.—J. F. B.

*Resin acids; Artificial —.* G. Cohn. Chem.-Zeit., 1916, 40, 725—727.

THE resinous acid condensation product from

formaldehyde and phenoxyacetic acid is typical of a whole group of compounds. The oxyacetic acids of cresol, guaiacol, carvacrol, resorcinol, etc., yield analogous substances; only the product derived from  $\alpha$ -naphthoxyacetic acid appears to be of a different type. It gives different colour reactions and its composition corresponds to that of a methylenedi- $\alpha$ -naphthoxyacetic acid. These resin acids may also be prepared by condensing alkali-soluble phenol-formaldehyde resins with chloroacetic acid. They contain the  $\text{O.CH}_2\text{COOH}$  group and have a high molecular weight. A mixture of 50 grms. of phenoxyacetic acid, 50 grms. of formaldehyde solution, and 20 grms. of strong hydrochloric acid is heated for 4 to 5 hours on the water-bath until the bulk of the acid has evaporated. The residual resin is kneaded with hot water and dried for about 10 hours on the water-bath (yield about 65 grms.). By reducing the proportion of formaldehyde to 1 mol. to 2 mols. of phenoxyacetic acid, soft resinous masses apparently containing unaltered phenoxyacetic acid are obtained. Increasing the proportion of formaldehyde has no effect on the results. Phenoxyacetic resin acid is soluble in acetone, methyl alcohol, amyl alcohol, terpineol, and glacial acetic acid, and sparingly soluble in alcohol, but insoluble or nearly so in benzene, chloroform, ether, carbon bisulphide, carbon tetrachloride, acetylene tetrachloride, and oil of turpentine. Fused with colophony it yields a homogeneous mass. It may be purified by dissolving it in water containing a trace of ammonia, filtering the solution, and re-precipitating the resin with glacial acetic acid. It gives a red coloration with strong sulphuric acid, and when heated with resorcinol and zinc chloride yields a deep-brown amorphous dyestuff, showing pronounced fluorescence in alkali solution. When treated with absolute alcohol and sulphuric acid it is converted into an amorphous ester, which is softer than the resin acid, and is readily soluble in acetone, sparingly soluble in methyl alcohol, and insoluble in dilute ammonia and sodium hydroxide solutions. It gives a red coloration with strong sulphuric acid. The resin acid is soluble in dilute sodium hydroxide solution, and the sodium salt is left as a vitreous residue on evaporating the solution. The ammonium salt may be obtained as an amorphous powder by evaporating the ammoniacal solution of the resin acid. Flocculent precipitates are obtained on adding solutions of the salts of heavy metals to the ammoniacal solution. For example, copper sulphate gives a greenish blue precipitate which dissolves in ammonia to an azure-blue solution. On adding a dilute solution of the ammonium or sodium salt to a solution of a basic dyestuff, such as Magenta, Methyl Violet, Methylene Blue or Malachite Green, and adding acetic acid, voluminous precipitates are obtained, the precipitation being quantitative under suitable conditions. The presence of a little hydrochloric acid does not interfere with the precipitation, which is attributed to adsorption of the dyestuff by the precipitated resin acid. Acid dyestuffs are not precipitated in this way. The ammonium salt also reacts with alkaloids, but antipyrine gives no precipitate. When heated at  $140^\circ\text{C}$ . for 30 mins. the resin acid lost 10 to 20% in weight and was converted into a soft porous mass, much less soluble in the ordinary solvents than the original resin acid. The resin acid produced by the interaction of trioxymethylene with phenoxyacetic acid and hydrochloric acid is a hard mass which does not melt again, but only softens a little when heated. When dried and powdered it forms a white powder which is only sparingly soluble in hot alcohol, methyl alcohol, and acetone. *Bakelite acetic resin acid* is obtained by condensing "bakelite A" with phenol and formaldehyde in presence of hexamethylenetetramine. Slight

variations in the conditions of preparation affect the properties of the acid. For example, some preparations melt at  $115^\circ\text{C}$ . whilst others remain unaltered at  $200^\circ\text{C}$ . It is insoluble in the usual organic solvents, but is fairly soluble in hot aniline. It gives an orange-red coloration with strong sulphuric acid, and with resorcinol yields a dyestuff. *Tricresoxyacetic resin acid* is prepared by heating together for 2 hours 50 parts of tricresol, 60 parts of chloroacetic acid, and 150 parts of 33% sodium hydroxide solution, and condensing the white product with an equal quantity of formalin and half the quantity of hydrochloric acid. The resulting resin acid is pale green, plastic while hot, but hard when cold. It is readily soluble in acetone, alcohol, methyl alcohol, pyridine, and dilute ammonia solution. It gives a deep brown-red coloration with sulphuric acid. *Resorcinol-di-acetic resin acid* is prepared in an analogous manner from resorcinoldiacetic acid. It is sparingly soluble in boiling acetone, and nearly insoluble in alcohol, ether, and glacial acetic acid. It gives a magenta coloration with sulphuric acid. *Guaiacolacetic resin acid* is soluble in cold acetone, hot alcohol and glacial acetic acid, insoluble in ether. It gives a red-violet coloration with sulphuric acid. The ammonium salt precipitates dyestuffs and alkaloids.  *$\alpha$ -Naphthoxyacetic resin acid* may be crystallised from glacial acetic acid. It melts at  $227^\circ$  to  $228^\circ\text{C}$ ., and gives a blue-green coloration and solution with strong sulphuric acid. It is readily soluble in hot acetone and alcohol, but only slightly soluble in ether.—C. A. M.

*Vulcanisation of gum resins.* Hutin. See XIV.

*Petrographic microscope in analysis.* Wright. See XXIII.

#### PATENTS.

*Pigment and paint; Aluminous*—. O. W. Pickering, Springfield, Mass., Assignor to Pickering Paint and Pigment Co., U.S. Pat. 1,195,604, Aug. 22, 1916. Date of appl., Oct. 10, 1914.

THE pigment consists of a substantially water-insoluble, flocculent metal aluminate, and the paint of a mixture of this and an oily vehicle, with or without driers.—E. W. L.

*Coating composition; Liquid*—. R. Picker, Assignor to Durlacque Manufacturing Co., St. Louis, Mo. U.S. Pat. 1,196,276, Aug. 29, 1916. Date of appl., June 26, 1914.

PONTIANAK gum copal, 90 lb., and shellac, 10 lb., are dissolved in alcohol, 14 galls., and benzol, 6 galls. Whiting may also be added.—E. W. L.

*Lead oxide; Process of carbonating*—. F. H. Sharpe, Liverpool. U.S. Pat. 1,196,595, Aug. 29, 1916. Date of appl., July 12, 1915.

SEE Eng. Pat. 17,579 of 1914; this J., 1915, 92.

*Lead oxide; Process and apparatus for carbonating*—. F. H. Sharpe. Fr. Pat. 479,219, July 7, 1915. SEE Eng. Pat. 17,579 of 1914; this J., 1915, 92.

*Calcium sulphate and zinc sulphide; Process for making a compound of*—. J. L. Carpenter. Fr. Pat. 478,289, Mar. 24, 1915.

SEE U.S. Pat. 1,146,690 of 1915; this J., 1915, 914.

*Varnish, lacquer, or the like and process of making same.* R. Gräter, Charlottenburg, Germany. U.S. Pat. 1,195,673, Aug. 22, 1916. Date of appl., Nov. 15, 1913.

SEE Fr. Pat. 464,617 of 1913; this J., 1914, 557.

*Rosin soap ; Method and apparatus for preparing dilute solutions of — containing dissolved unsaponified rosin.* R. J. Marx and J. A. de Cew. Fr. Pat. 478,830, Feb. 20, 1915.

SEE Eng. Pat. 2142 of 1915 ; this J., 1916, 317.

#### XIV.—INDIA-RUBBER ; GUTTA-PERCHA.

*Vulcanisation of caoutchouc ; Chemical investigation of the — and the possibility of its regeneration from the vulcanised product.* II. C. Harries and E. Fonrobert. Ber., 1916, 49, 1390—1398. (See this J., 1916, 747.)

VULCANISATION OF Para rubber with 10% of sulphur for 30 minutes at 145° C. gives a product which, when exhaustively extracted (for 60 days) with acetone, contains only 0.20% of sulphur. The extracted product is less elastic than the unvulcanised rubber and does not give a satisfactory product on further vulcanisation. It is therefore another modification of the unvulcanised rubber, the sulphur present being regarded by the authors as negligible. The hydrochloride prepared from the unextracted product is similar in appearance to that derived from unvulcanised rubber, but is harder, and is insoluble in the usual solvents. Hydrochloric acid is split off at 155° C., 10° C. higher than in the case of the hydrochloride from unvulcanised rubber. Vulcanisation of the same mixing for 3 hours gives a product containing, after exhaustive extraction, 2% of sulphur. Commercial vulcanised rubber always contains some rubber which yields a soluble hydrochloride ; in red motor tyres, for example, this amounted to 20% of the whole. The "reclaimed rubber" obtained by decomposing this hydrochloride with pyridine, however, differed from the original unvulcanised rubber in that its ozonide yielded diacetylpropane on hydrolysis, indicating a change in position of the double bond. The sulphur present in the insoluble hydrochloride remains in the reclaimed rubber prepared by the action of pyridine. That there is no structural alteration in the molecule during vulcanisation is demonstrated by the fact that the ozonide of vulcanised Para rubber gave only traces of methyleyclohexenone on hydrolysis. The acetone-extracted vulcanisate was ozonised with difficulty and the oxyozonide formed gave much acid and little aldehyde on hydrolysis. Natural rubber gave the same products as highly purified caoutchouc, but was slightly less readily attacked by ozone in ethyl acetate solution. The change brought about by vulcanisation is apparently one in the size of the molecule.—E. W. L.

*Rubber thread ; Physical and chemical analysis of —.* A. Dubosc. Caout. et Gutta-percha, 1916, 13, 9007—9008.

THE use of rubber thread has undergone considerable expansion during the war owing to its employment in shock-absorbers, catapults, etc., and in view of its importance analyses were made of a number of samples. The results were as follows :—

Sample No.	1.	2.	3.	4.	5.	6.	7.
Dimensions, mm.	0.80×0.82	0.70×0.70	0.80×0.60	0.60×0.60	0.66×0.68	0.70×0.70	0.60×0.60
Tensile strength, grms. per sq. mm.	693	606	717	717	483	594	669
Elongation (times original length)	12.4	12.7	12.5	12.5	12.6	11.9	10.4
Elastic limit (times original length)	3.5	4.9	3.7	3.4	3.7	3.6	4.0
Acetone extract (per cent.)	2.30	3.30	2.25	2.38	1.87	2.37	3.61
Moisture	0.72	0.85	0.85	0.92	0.73	0.98	0.99
Ash	2.51	2.73	1.84	2.19	1.75	2.26	2.48
Total sulphur	2.77	2.77	3.04	2.84	2.68	2.95	2.75
Chloroform extract	1.50	1.00	4.20	0.80	7.02	1.75	1.01
Alcoholic potash extract	0.13	0.08	0.03	0.11	0.13	0.05	0.14
Caoutchouc	90.07	88.69	87.79	90.77	89.23	89.65	89.23

In sample 5 the high chloroform extract and low tensile strength are noteworthy. The ash consists in each case mainly of talc, used in manipulating the rubber before vulcanisation.—E. W. L.

*Gum-resins ; Vulcanisation of —.* Hutin. Caout. et Gutta-percha, 1916, 13, 9025—9026.

It has been found that the addition of gum-resins, such as shellac, to ebonite mixings, retards the cure, and gives a product which does not polish well. The gum-resins can, however, be vulcanised, and, if added to the mixing in the vulcanised form, give satisfactory results. Shellac can be vulcanised by mixing 93 parts with 7 parts of sulphur and heating for 12 hours—including 2 hours "rise"—at 65—70 lb. steam pressure. The minimum temperature for vulcanisation is that corresponding with 50—55 lb. steam pressure, a preliminary decomposition of the shellac taking place with the formation of an unsaturated compound capable of combining with sulphur. The fully vulcanised product is insoluble in acetone. Copal and sandarac give similar results. Colophony does not vulcanise.—E. W. L.

*Sun-cracking [of rubber] ; C. O. Weber's test for —. [Acetone peroxide.]* D. F. Twiss. India-Rubber J., 1916, 52, 325.

THE mixture of acetone with an aqueous solution of hydrogen peroxide, the use of which is recommended by Weber for the determination of liability to "sun-cracking" in vulcanised rubber goods, may, after keeping for a month or so, deposit compact colourless crystals of acetone peroxide,  $C_6H_{10}O_8$  (Wolffenstein, Ber., 1895, 28, 2265). Although this substance can be melted with safety (at 97° C.), it is capable of exploding with great violence when subjected to shock, or if heated above its melting-point, and great care should therefore be taken to prevent its accumulation in any quantity, especially in a dry condition. 0.03 grm. of the substance, when heated in an open test-tube, will explode with such force as to shatter the tube.—E. W. L.

*Some aspects of the synthesis of caoutchouc.* Luff. See page 983.

*Raw materials used by the rubber manufacturer.* Porritt. See page 986.

#### PATENTS.

*Plasticity of rubber and rubber mixings ; Apparatus for and method of measuring —.* H. H. Grundy and P. Schidrowitz, London. Eng. Pat. 15,438, Nov. 2, 1915.

THE degree of plasticity of rubber or rubber mixings is ascertained by measuring the electrical power consumed over a time interval during the mixing and masticating operations. This may be done by observations of an electricity meter from time to time, or by a drum meter recording the consumption on a curve. The latter has a definite relationship to the degree of plasticity, and a device may be used for signalling the position of the curve by means of a bell or similar apparatus. As an alternative, two index hands may be used on one

dial of the meter, one hand moving, independently of the meter, at a uniform speed corresponding to the speed of the meter hand when the proper degree of plasticity is obtained.—B. N.

*Rubber; Process of reclaiming* — H. O. Chute, New York. U.S. Pat. 1,196,334, Aug. 29, 1916. Date of appl., June 3, 1913.

SCRAP rubber is heated below the vulcanising temperature, first in a solution of halogen acid, alone or in presence of a soluble halide, such as calcium chloride; or in a mixture of sulphuric acid and excess of a solution of a chloride; and then in a solution of caustic alkali. The alkali is then removed, and the rubber rendered plastic by heating with water at a high temperature.—E. W. L.

*Rubber goods; Eliminating porosity in* — W. J. Mellersh-Jackson, London. From Boston Rubber Shoe Co., Malden, Mass., U.S.A. Eng. Pat. 16,226, Nov. 17, 1915.

SEE U.S. Pat. 1,164,860 of 1915; this J., 1916, 264.

*Rubber from rubbered fabrics, especially tyres; Recovery of* — C. de Villers. Fr. Pat. 478,280, July 11, 1914.

SEE Eng. Pat. 10,146 of 1915; this J., 1916, 934.

*Rubber sponge; Manufacture of* — P. Schidrowitz and H. A. Goldsbrough. Fr. Pat. 478,369, Apr. 13, 1915.

SEE Eng. Pat. 1111 of 1914; this J., 1915, 624.

*Impregnating textile belts or the like with gutta-percha, balata, or rubber.* Eng. Pat. 101,127. See V.

## XV.—LEATHER; BONE; HORN; GLUE.

*Leather; Chemical and microscopical examination of* — E. Seel and A. Sander. Z. angew. Chem., 1916, 29, 325—326, 333—334.

MOST of the reactions which have been proposed for the detection of the synthetic tanning agent Neradol in leather are either not sufficiently sensitive or are rendered ineffective by the presence of other tanning materials. The authors have found the following hydroxyazo and indophenol reactions satisfactory for the detection of Neradol D. 20 grms. of the leather, in small pieces, is boiled with 250 c.c. of water for  $\frac{1}{2}$ — $\frac{3}{4}$  hour, and 100 c.c. of the hot filtered solution is treated with 20 c.c. of a mixture of equal parts of 40% formaldehyde, concentrated hydrochloric acid, and water (compare Stiasny, this J., 1906, 275), and boiled for  $\frac{1}{2}$  hour under a reflux condenser. After cooling, the solution is filtered and concentrated, preferably after a preliminary purification by dialysis. An alternative method of treating the leather infusion consists in treating it with lime water, or neutralising it with ammonia and treating it with a calcium salt, and then filtering and concentrating. *Hydroxyazo reaction.* 5 c.c. of the concentrated solution is treated with excess of alkali, cooled with ice, mixed with about half its volume of alcohol, and three or four drops of a solution of diazotised *p*-aminophenol added. A blue coloration indicates the presence of Neradol D. If the blue colour does not appear immediately, the solution is acidified with hydrochloric acid, shaken vigorously with ether, the ethereal solution separated and added to water, and then sodium hydroxide added, when a dark bluish-green colour appears at the surface of contact of the two layers if Neradol D be present. *Indophenol reaction.* 5 c.c. of the concentrated aqueous extract of the leather is treated with a drop of a solution of the hydrochloride of dimethyl-

phenylenediamine (obtained by reduction of Methyl Orange), the mixture is made alkaline with caustic soda, and treated with one or two drops of a 5% solution of potassium ferricyanide: a blue coloration indicates the presence of Neradol D. The test is rendered more sensitive if alcohol be introduced to form an upper layer before adding the ferricyanide: a blue ring forms slowly at the surface of contact and gradually extends into the alcohol layer. Neradol ND (prepared by condensation of naphthalene- $\beta$ -sulphonic acid and formaldehyde), not being a phenolic compound, does not give either of the above reactions directly, but responds to both after oxidation with sodium hypochlorite solution.

For staining sections of leather for microscopical examination, in order to ascertain whether the skin has been tanned completely through, the best results were obtained with Malachite Green, Brilliant Green, Methyl Green, Bismarck Brown, and Rhodamine, all of which dye the leather whilst leaving the untanned skin unaffected. By dyeing first with a basic dyestuff, washing with water and alcohol, and then again dyeing with an acid dyestuff, the untanned skin and the leather may be stained different colours: specially effective results were obtained with combinations of Brilliant Green and Eosin and of Rhodamine and Patent Blue.—A. S.

*Sole leather tests with Australian pine barks; Comparative* — F. A. Coombs. Collegium (London), 1916, 205—215.

SYSTEMATIC tanning experiments were carried out with Australian pine bark liquors, wattle bark liquors, and liquors made from five-sixths wattle bark and one-sixth myrobalans and valonia. Precautions were taken to make the tests strictly comparative by selecting similar hide pieces, using the same liming process, tanning in liquors of corresponding specific gravity, etc. The leather made with pine bark showed the highest degree of tannage, though the rate of penetration of tannin was slower. It also proved to be more resistant to water than the other leathers, at least in the unrolled condition.—F. C. T.

*Chrome-tanned leather; Determination of chromic oxide in* — M. C. Lamb and A. Harvey. Collegium (London), 1916, 201—203.

THE presence of iron sometimes leads to too high results in the estimation of chromium. To remove the iron, it is best to fuse the leather ash with sodium peroxide and subsequently treat with water, not acid, when ferric oxide remains undissolved and may be filtered off. The percentage of chromic oxide should be calculated on the weight of degreased leather and not on the original material. The degreased leather should contain at least 2.8—3.0% of chromic oxide or it will be found to be undertanned.—F. C. T.

*Deterioration of leather used in gas meters.* Lamb. See page 989.

### PATENTS.

*Bronze kid [leather]; Producing* — A. G. Bloxam, London. From A. Combe et Fils et Cie., Paris. Eng. Pat. 101,109, Feb. 21, 1916. (Appl. No. 2575 of 1916.)

BRONZE kid is produced by the aid of Magenta and allied colouring matters, the dyeing operation being followed by smoothing and topping operations. The dyeing and topping liquors are prepared from crystallised Magenta and "Violet" and tannic acid dissolved in 90% alcohol, nitrobenzene being also added to the dyeing liquor, and resin, used as a varnish, added to the topping liquor. The process may be applied as a finishing operation to leather, the final polishing being

facilitated by the addition of amyl alcohol to the topping liquor, or it may be used for staining or maintaining the colour of boots and shoes.—B. N.

*Gelatinous substances; Production of solid*—. E. Salm. Assignor to A.-G. für Chem. Produkte vorm. H. Scheidemann, Berlin. U.S. Pat. 1,195,099, Aug. 15, 1916. Date of appl. Feb. 15, 1916.

SOLID gelatinous substances are obtained in a divided condition by bringing them, when in the liquid state, into contact with a non-volatile oil of sp.gr. 0.8 to 1.2. The globules of glue are removed by a mechanical device as they are formed, and then washed by benzene or the like, which is afterwards recovered; the globules are dried in a warm room.—B. N.

*Tanning hides and skins; Process and apparatus for*—. E. Wilson. Fr. Pat. 478,138, Mar. 24, 1915.

SEE Eng. Pat. 7762 of 1914; this J., 1915, 437.

*Tanning extracts; Production of*—. W. E. Horrocks and J. K. Tullis. Fr. Pat. 479,426, July 31, 1915.

SEE Eng. Pat. 18,332 of 1914; this J., 1915, 1062.

## XVI.—SOILS; FERTILISERS.

*Fifty-second annual report on alkali, etc., works, by the Chief Inspector, 1915.* See VII.

*Petrographic microscope in analysis.* Wright. See XXIII.

### PATENTS.

*Phosphatic fertilisers; Manufacture of*—. A. Dickson. Fr. Pat. 478,707, Sept. 7, 1914.

SEE Eng. Pat. 18,999 of 1913; this J., 1914, 1067.

*Composition and process for treating plants.* U.S. Pat. 1,194,608. See XIX.B.

## XVII.—SUGARS; STARCHES; GUMS.

*White [cane] sugar manufacture; Study of the syrup precipitate in*—. C. E. Coates and L. C. Slater. J. Ind. Eng. Chem., 1916, 8, 789—792.

IN the direct sulphitation process for the manufacture of white cane sugar, a precipitate, difficult to remove by filtration, is formed when the hot syrup is allowed to stand. The authors examined two specimens of this precipitate. One specimen was obtained from a factory in which phosphoric acid is added to the filtered juice before concentration and the other from a factory in which no phosphoric acid is used: the dried precipitates consisted largely of organic matter and silica, together with calcium phosphate in that from the factory using phosphoric acid; copper was present in both cases. The organic matter appears to be chiefly calcium salts of organic acids. It is estimated that the amount of dry precipitate is less than 0.01% of the weight of syrup, and the best method of dealing with it appears to be to allow the hot syrup to settle for at least 4 hours in tanks sheathed to prevent radiation as far as possible, then decant the syrup, and add the "bottoms" to the limed juice previous to filtration.—A. S.

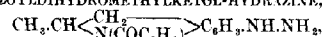
*Dextrose; Action of hydrogen sulphide on*—. W. Schneider. Ber., 1916, 49, 1638—1643.

WHEN hydrogen sulphide is passed into a solution of dextrose in pyridine, with every precaution for the expulsion and exclusion of air and with repeated renewal of the supply of gas over a period of 22 days, combination takes place and a syrupy residue is left after removal of the excess of hydrogen sulphide and most of the pyridine by distillation under reduced pressure. By means of an anhydrous solution of ammoniacal silver nitrate in pyridine, the thioglucose derivative is precipitated in the form of its silver compound,

insoluble in a mixture of alcohol and pyridine. This compound resembles the similar derivative prepared from sinigrin and analogous synthetic thiourethaneglucosides. It is an amorphous pale yellow powder, very soluble in water, insoluble in alcohol and ether; it dissolves in cold pyridine but is precipitated in a flocculent form on warming; it melts at about 144°C. and is readily decomposed by hydrogen sulphide with separation of silver sulphide. It differs, however, from the derivative prepared from the glucosides in its higher proportion of sulphur, and it would appear that the product of the direct action of hydrogen sulphide on dextrose is a mixture of about 2 parts of monothioglucose with 1 part of dithioglucose.—J. F. B.

*Galactose; Benzoyldihydromethylketol-hydrazine, a new reagent for*—. J. von Braun. Ber., 1916, 49, 1266—1268.

BENZOYLDIHYDROMETHYLKETOL-HYDRAZINE,



is a specific reagent for galactose, with solutions of which it gives a colourless crystalline precipitate in from  $\frac{1}{2}$  to 2 hours according to the concentration. With dextrose, levulose, mannose, arabinose, and xylose no precipitate is produced. The base is prepared from benzoyldihydromethylketol, which is nitrated and reduced to *m*-amino-*N*-benzoyldihydromethylketol. This is diazotised and reduced with stannous chloride, and the hydrazine isolated in the usual way. It crystallises from alcohol in colourless needles, m.pt. 150—151°C., and is apparently quite stable when dry. The hydrochloride melts at 197°C., and the semicarbazide derivative at 213°C.—G. F. M.

*Petrographic microscope in analysis.* Wright. See XXIII.

### PATENT.

*Starch products; Manufacture of*—. A. S. Hoyt. Fr. Pat. 479,236, July 9, 1915.

SEE U.S. Pat. 1,148,453 and 1,148,454 of 1915; this J., 1915, 917.

## XVIII.—FERMENTATION INDUSTRIES.

*Glycylglycine; Kinetics of enzymic hydrolysis of*—. K. G. Demby. Comptes rend. Trav. Lab. Carlsberg, 1916, 11, 263—295.

THE optimum reaction for the hydrolysis of glycylglycine by the creptase of yeast is  $pH=7.8$ . The concentration of hydrogen ions diminishes continuously during hydrolysis, owing to a difference between the electrolytic dissociation constants of the substrate and of the product; and this change affects the activity of the enzyme and therefore the course of the action. If the reaction of the medium is maintained constant, by addition of phosphate "buffer" salts, hydrolysis proceeds as a unimolecular reaction, provided sufficient enzyme is present to render losses due to auto-digestion negligible. In alkaline liquids, and even at the optimum reaction, the activity of the enzyme is slowly destroyed, but glycylglycine exerts a protective influence. Glycine and the ions K, Na, Cl, Br, F, SO<sub>4</sub>, and NO<sub>3</sub> have no influence on the enzyme, at low concentrations, but chlorates have a retarding action and cyanides act as powerful poisons.—J. H. L.

### PATENT.

*Agave plant; Process of treating the juices of the* — [preparatory to fermentation]. L. Lavedan. New Orleans, U.S.A. Eng. Pat. 101,281, Apr. 19, 1916. (Appl. No. 5762 of 1916.)

SEE U.S. Pat. 1,182,691 of 1916; this J., 1916, 704.



## XIXA.—FOODS.

*Bread making; Use of certain yeast nutriment in*  
— H. A. Kohman, C. Hoffman, T. M. Godfrey,  
L. H. Ashe, and A. E. Blake. *J. Ind. Eng. Chem.*,  
1916, 8, 781—789.

THE rate of fermentation in bread making is markedly accelerated by small quantities of ammonium and calcium salts, so that it is possible to use considerably less yeast than usual and yet obtain equally good results as regards size of loaf, whilst the colour and texture of the bread are improved. If a small quantity of potassium bromate be added, the quantity of yeast may be still further reduced. The ammonium and calcium salts act chiefly as yeast nutriment or stimulants, whilst the potassium bromate exerts a marked ageing or maturing effect on the dough, due to its oxidising power; a similar but less pronounced ageing effect is produced by passing oxygen through the dough. If ammonium chloride, calcium sulphate or chloride, and potassium bromate be used together, from 50 to 65% of the usual quantity of yeast can be saved, and this results in a saving of about 2% of fermentable carbohydrates, calculated upon the total flour used, due to the diminished consumption of these by the yeast. The use of these salts, moreover, ensures more uniform results as to quality of bread in different localities irrespective of the character of the local water supply. In practice the salts are dissolved in the water used in the dough batch, about 2 oz. of a calcium salt, a little less than 1 oz. of ammonium chloride, and 0.02 oz. of potassium bromate being used per 60 lb. of water or per 160 lb. of bread. The process has been used successfully with different kinds and grades of flour and in the manufacture of different kinds of bread.

A suggested method of utilising stale bread consists in "cooking" it and then digesting with malt. The gluten remains in flakes and can be separated by filtration from the sugars formed by hydrolysis of the starch. Glutamic acid hydrochloride can be obtained by digesting the gluten residue with concentrated hydrochloric acid, and is of value both as a yeast stimulant and for its ageing or maturing effect on dough.—A. S.

*Milk; Comparison of the bacterial count with the sediment or dirt test of* — H. C. Campbell.  
*U.S. Dept. Agric., Bull. No. 361, 1916, 1—6.*

THE quantity of sediment or dirt collected when milk is filtered through a cotton disc is no criterion of the number of bacteria present in the milk, and, consequently, gives no indication of the hygienic conditions under which the milk has been produced. For instance, a milk showing but little, if any, sediment or dirt, may contain up to one million bacteria per c.c., whilst the number of bacteria in a dirty milk may be as low as 7000 per c.c. Since the sediment test has been used in factories, etc., for controlling the quality of milk, producers have begun to strain the milk, and the test is now of little value, except for the detection of actual dirt in a sample.—W. P. S.

*Casein; Influence of ethyl alcohol and glycerol on the rate of solution of* — by sodium hydroxide.  
T. B. Robertson and K. Miyake. *J. Biol. Chem.*,  
1916, 26, 129—142.

ALCOHOL and glycerol retard the penetration of casein particles by 0.016N sodium hydroxide solution. The penetration formula  $x = Kt^m$  (see this J., 1916, 939) expresses the relationship between the quantity of casein dissolved and the time of stirring in all glycerol-water mixtures and in alcohol-water mixtures containing less than 4.5 gm.-mols. or more than 7 gm.-mols. alcohol per litre, but the formula does not apply to the rate of solution of casein in 0.016N sodium hydroxide solution containing between 4 and 8 gm.-mols.

alcohol per litre. In these mixtures the initial solution of the casein is succeeded, after prolonged stirring, by partial re-precipitation. In concentrations below 4.5 gm.-mols. per litre the coefficient of penetration decreases, with negative acceleration (*loc. cit.*), as the concentration of alcohol increases; in concentrations above 7 gm.-mols. per litre the coefficient decreases, with positive acceleration, as the concentration of alcohol increases. The relationship of the magnitude of the coefficient of penetration to the concentration of alcohol is indeterminate in the case of mixtures containing between 4.5 and 7 gm.-mols. alcohol per litre.

It is inferred that in concentrations of alcohol below 4.5 gm.-mols. per litre, the casein molecules in the presence of 0.016N sodium hydroxide solution are all of the single type, whilst at concentrations above 7 gm.-mols. they are practically all of a polymerised type. With intermediate concentrations of alcohol, the proportion of polymerised molecules to single molecules progressively increases with the alcoholic concentration.—W. P. S.

*Proteins; Origin of the humin nitrogen formed by the acid hydrolysis of* — Hydrolysis in the presence of carbohydrates and of aldehydes. R. A. Gortner. *J. Biol. Chem.*, 1916, 26, 177—204.

GORTNER and Blish have stated previously (*J. Amer. Chem. Soc.*, 1915, 37, 1630) that in all probability the humin nitrogen of protein hydrolysis has its origin in the tryptophane nucleus, a statement to which exception has been taken by other workers. The author now shows that the humin nitrogen is greatly increased when the hydrolysis is carried out in the presence of a carbohydrate, whilst the amount of ammonia nitrogen is not materially altered. Tryptophane cannot be determined accurately by hydrolysing proteins in the presence of carbohydrates; if the quantity of carbohydrate greatly exceeds that of the protein, the distribution of the nitrogen cannot be determined accurately by Van Slyke's method (this J., 1911, 771, 1135). When fibrin is hydrolysed in the presence of furfural, the humin nitrogen is increased; this may be due to the absorption or occlusion of other amino-acid nitrogen by the humin. A black, insoluble mass is obtained by boiling furfural with concentrated hydrochloric acid and it is possible that the humin, derived from carbohydrates, is actually formed from furfural, which is in turn formed from carbohydrates. The quantity of humin nitrogen also increases when fibrin is hydrolysed in the presence of benzaldehyde or of small quantities of formaldehyde; large quantities of the latter decrease the yield of humin nitrogen. Both tryptophane and tyrosine yield a considerable proportion of "acid-insoluble" humin nitrogen when boiled with hydrochloric acid in the presence of benzaldehyde; when tryptophane is hydrolysed in the presence of formaldehyde, a considerable part of the nitrogen is retained in the "acid-insoluble" humin, but a similar hydrolysis of tyrosine does not yield an "acid-insoluble" humin.—W. P. S.

*Proteins; Behaviour of purified* — towards proteolytic enzymes. E. M. Frankel. *J. Biol. Chem.*, 1916, 26, 31—59.

IN pepsin-hydrochloric acid digestion the pepsin is the effective agent; hydrochloric acid alone, in the concentrations usually employed, has very little proteolytic action on proteins. Experimental evidence was obtained that there is, during digestion, a parallelism in the cleavage curves of egg-albumin, casein, cottonseed globulin, edestin, gelatin, coagulated lactalbumin, phaseolin, soya bean globulin, squash-seed globulin, amandin, conglutin, and legumelin, if the cleavage is calculated as the ratio of the amino nitrogen liberated at any one time to that obtained by total hydro-

lysis of the protein with concentrated acid. The results obtained in proteolysis are comparable only when the substrates are in solution; otherwise, differences of 10 to 15% may be obtained in duplicate experiments. Pepsin-hydrochloric acid can liberate about 20% of the total amino nitrogen of a protein within 100 hours; trypsin acting on proteins partially digested with pepsin effects a cleavage of about 70%. The action of trypsin on native proteins causes a cleavage of about 50% of the peptide linkages; further addition of trypsin may cause increased disintegration of the protein. Erepsin following the action of pepsin may cause a cleavage of about 85% of the protein, whilst the successive action of pepsin, trypsin, and erepsin liberates about 90% of the total amino nitrogen of the protein.—W. P. S.

*Trypsin; Dialysis of— and the proteoclastic action of the protein cleavage products.* C. Funk. *J. Biol. Chem.*, 1916, 26, 121—128.

THE author has repeated certain experiments described by Herzfeld (this J., 1915, 811) and finds that trypsin, when subjected to dialysis in collodion bags, loses a large part of its amino-nitrogen, corresponding with the passage of the amino-acids into the dialysate. The latter has no hydrolysing action on proteins, whilst the residue has distinct proteoclastic properties. The diminution of amino-nitrogen, when the dialysate is allowed to act on proteins, is possibly due to the adsorption of a certain quantity of the cleavage products by the membrane, or by the protein substrate, and is apparently not due to synthetic action. Glycine, glycylglycine, *l*-leucine, and *l*-alanyl-*d*-alanine do not hydrolyse proteins, as an increase of amino-nitrogen is never found; occasionally, an increase in the total nitrogen is observed, for which an explanation cannot be offered.—W. P. S.

*Hydric acid (benzoic and m-cresotic acids); Hygienic influence of—.* K. B. Lehmann. *Chem.-Zeit.*, 1916, 40, 725.

HYDRIC acid is composed of a mixture in equal parts of benzoic and *m*-cresotic acids, and is used as a preservative for marmalade, etc. Practical tests in which four persons ate 100 grms. of marmalade containing 0.25 gm. of the preservative daily for 14 days, caused no unpleasant effects. The conclusion is drawn from these results and from theoretical considerations that no injury to health need be feared from the use of marmalade containing 0.2 to 0.25% of hydric acid.—C. A. M.

*Kinetics of enzymic hydrolysis of glycylglycine.* Derby. See XVIII.

#### PATENTS.

*Artificial milk; Manufacture of— and the treatment of its residues.* W. J. Melhuish, Upper Parkstone, Dorset. Eng. Pat. 13,903, Sept. 30, 1915.

EARTH nuts, pine kernels, pine nuts, or palm nuts are ground and the meal is treated with hot water containing added alkali salts and malto-dextrin. The aqueous portion is then strained off, a further quantity of salts, and fatty acids (including butyric acid) are added, the liquid is treated with lactic bacteria, then pasteurised, and cooled. The resulting product resembles ordinary milk in appearance; the quantities of water, nuts, etc., used are such that the final liquid contains about 13% of total solids. The liquid may be concentrated to any desired consistence, or dried to a powder; if a butter "starter" is added, the liquid may be used in the manufacture of margarine. A product resembling cream is obtained by emulsifying the liquid with any desired fat, treating the mixture with milk bacteria, and pasteurising it; the addition of butyric acid may be omitted and the liquid treated with lactic bacteria to obtain a milk having a nutty flavour.

The residue of nut meal obtained in the process may be dried, roasted, and mixed with other foodstuffs. (See also Eng. Pat. 24,572 of 1913; this J., 1915, 196.)—W. P. S.

*Milk and other liquids; Apparatus for sterilising—.* M. M. Pfeiff, Fullerssta, Sweden. Eng. Pat. 100,692, June 14, 1916. (Appl. No. 8428 of 1916.) Under Int. Conv., June 16, 1915.

THE apparatus comprises a rectangular tank having double upper walls, the tank, and the space between the double walls, being nearly filled with water which is heated to boiling. An inclined cover fits into the top of the tank at a level below that of the water in the double walls; the milk or other liquid is admitted to the upper end of this cover, flows to the lower end and thence through a channel extending round three sides of the tank and adjacent to the inner part of the double wall. Perforated transverse plates are provided in the cover and in the channel for the purpose of mixing the milk during its passage. The milk is discharged from the channel into suitable receptacles.—W. P. S.

*Alfalfa (Lucerne) extract. Alfalfa products.* M. C. Rich, Bellefourche, S.D., Assignor to The American Alfalfa Products Co., Denver, Colo. U.S. Pats. (A) 1,195,152, (B) 1,192,153, and (C) 1,195,154, Aug. 15, 1916. Dates of appl., (A) and (B) May 15, and (C) May 17, 1915.

(A) ALFALFA, which is naturally free from woody fibre, and from which woody hairs, secretions, and impurities have been removed, is infused with alcohol, and the infusion filtered and concentrated. (B) To render alfalfa fit for human consumption, it is cut before it has become woody and fibrous, then washed to remove impurities, heated to prevent bleaching, and ground to a flour. (C) Alfalfa, which is naturally free from woody fibre and which has been washed to remove impurities, is mixed with a saccharine material and the mixture heated sufficiently to caramelize it. The mass is then extracted, and the extract mixed with gelatin or concentrated by evaporation.—J. H. J.

*Hydrogenated oil food products.* A. Lowenstein, Chicago, Ill. U.S. Pat. 1,187,999, June 20, 1916. Date of appl., Aug. 31, 1915.

COTTONSEED or other oil is catalytically hydrogenated until non-glyceridic constituents (e.g., those giving Halphen's or Millian's reactions) are modified or destroyed, the process being stopped before the solidifying point has been raised more than 0.1° to 0.5° C. Oil thus treated will keep much better than ordinary cottonseed oil or other fatty oils, while the dissolved "stearin" crystallises readily.—C. A. M.

*Food products; Preparation of—.* M. Franzén. Fr. Pat. 477,949, Feb. 17, 1915.

SEE Eng. Pat. 2607 of 1915; this J., 1916, 324.

*Flour; Treatment of—.* W. G. Andrews and F. D. Larabee. Fr. Pat. 478,292, Apr. 1, 1915.

SEE Eng. Pat. 2466 of 1915; this J., 1915, 884.

*Pectous alimentary product, and process for extracting it from fruits and legumes.* R. Douglas. Fr. Pat. 478,608, May 5, 1915.

SEE Eng. Pat. 6497 of 1915; this J., 1916, 614.

*Alimentary and similar products; Concentrated—.* Techno-Chemical Laboratories, Ltd. Fr. Pat. 479,000, June 11, 1915.

SEE Eng. Pat. 14,671 of 1914; this J., 1915, 848.

*Chocolate or soluble cocoa powder; Manufacture of—.* J. Gloor. Fr. Pat. 479,067, June 19, 1915.

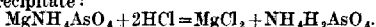
SEE Eng. Pat. 7041 of 1915; this J., 1916, 378.

*Grinding machine [for oil-seeds, etc.].* Eng. Pat. 12,015. See I.

**XIXs.—WATER PURIFICATION; SANITATION.**

*Mineral water; Analysis of — by volumetric methods. [Determination of magnesium.]* E. B. Jensen. Proc. Australasian Inst. Min. Eng., 1916, 75—98.

Two methods are described for the volumetric determination of magnesium in waters. In the first, the magnesium, after removal of calcium, is precipitated as ammonium magnesium arsenate, which is collected, washed with dilute ammonia, then with 50% alcohol, dissolved in a known volume of *N*/10 hydrochloric acid, and the excess of acid titrated with sodium carbonate solution, using methyl orange as indicator. The quantity of magnesium present is calculated from the volume of hydrochloric acid neutralised by the precipitate:



In the second method, the ammonium magnesium arsenate precipitate is digested for two hours with sulphurous acid to reduce the arsenate to arsenite, the solution then boiled to expel sulphur dioxide, cooled, neutralised with sodium hydroxide, using phenolphthalein as indicator, next rendered slightly acid with tartaric acid, treated with an excess of sodium bicarbonate, and titrated with standard iodine solution; 1 c.c. of *N*/10 iodine solution is equivalent to 0.0012 gm. of magnesium. Both methods yield accurate results.—W. P. S.

*Lime-sulphur solutions; Determination of thio-sulphate sulphur in — by iodine titration.* P. R. Blumenthal and S. D. Averitt. J. Amer. Chem. Soc., 1916, 38, 1701—1704.

TETRATHONATE is oxidised to sulphate by excess of iodine in neutral or faintly acid solutions, on standing, but the amount which can be thus oxidised in an ordinary iodine titration does not cause an appreciable error in the determination of thiosulphate. The iodine values obtained by titrating lime-sulphur solutions, after decomposing polysulphides by hydrochloric acid and expelling hydrogen sulphide by boiling, actually represent the thiosulphate content, for the results agree closely with those obtained by oxidising the solutions with bromine, after the titration, and precipitating with barium chloride. If sulphates were present the thiosulphate figures by iodine titration would be higher than those obtained by weighing the barium sulphate, whereas actually the gravimetric results were slightly higher than those obtained volumetrically.—A. S.

*Methylheptenone as an insecticide.* Perfum. and Essent. Oil Rec., 1916, 7, 295.

THE efficacy of lemongrass oil as an insecticide has been traced to the presence of methylheptenone in the oil. Lemongrass oil contains only a relatively small proportion of methylheptenone, but the latter can be readily prepared by the action of alkali on citral, and experiments have shown that it is much more effective than anisol as an insecticide.

*Use of solutions of borax and boric acid in the colorimetric determination of the concentration of hydrogen ions in sea water.* Palitzsch. See XXIII.

**PATENTS.**

*Water; Process for the purification of —.* P. W. Oerolt, Sutton-on-Sea. Eng. Pat. 11,922, Aug. 18, 1915.

FERRIC hydroxide is deposited on asbestos wool, and the latter is then lightly packed into a tube, which is fitted to the outlet nozzle of the receptacle containing the water to be treated. The water that comes through the filter is quite free from arsenic. The tube is cleaned out from time to time and refilled with asbestos on which ferric hydroxide has been deposited. The apparatus is suitable for field use.—J. H. J.

*Plants; Composition and process for treating —.* C. W. Eastman, Great Falls, Mont. U.S. Pat. 1,194,608, Aug. 15, 1916. Date of appl., Nov. 27, 1915.

THE plant is sprayed with a solution containing an arsenical insecticide, a bichromate, and dextrin. Under the influence of light, the bichromate and the dextrin interact to produce an insoluble compound, which forms a closely adherent coating on the plant, and maintains the arsenical insecticide in close contact therewith.—J. H. J.

*Water; Softening of —.* R. Gans, Assignor to J. D. Riedel A.-G., Berlin. U.S. Pat. 1,195,923, Aug. 22, 1916. Date of appl., Aug. 5, 1911. Renewed Mar. 26, 1915.

SEE Eng. Pat. 3870 of 1911; this J., 1912, 356.

*Water; Purification, clarification, and sterilisation of —.* H. Neel. Fr. Pat. 479,154, Nov. 7, 1914. SEE Eng. Pat. 19,722 of 1914; this J., 1915, 1163.

*Water; Apparatus for softening, sterilising, and otherwise treating —.* H. J. Magrath. Fr. Pat. 479,455, Aug. 3, 1915.

SEE Eng. Pat. 18,867 of 1914; this J., 1915, 1030.

*Sterilisation of liquids.* P. H. Dawe. Fr. Pat. 479,657, Apr. 17, 1915.

SEE Eng. Pat. 9567 of 1914; this J., 1915, 631.

**XX.—ORGANIC PRODUCTS; MEDICINAL SUBSTANCES; ESSENTIAL OILS.**

*Thebaine, and phenyldihydrothebaine; Reduction of —.* M. Freund and E. Speyer. Ber., 1916, 49, 1287—1307.

THE investigation of phenyldihydrothebaine, which from its manner of preparation must be regarded as having the same structure as the alkaloid itself, leads to the conclusion that no aliphatic double bonds are present as suggested by Knorr's formula (compare this J., 1907, 943), since it completely resisted reduction by the ordinary methods both in acid and alkaline solution. The absorption of 1 mol. of hydrogen was observed in presence of colloidal palladium, but the product was a secondary base,  $(\text{C}_{24}\text{H}_{25}\text{O}_2)\text{NH}\cdot\text{CH}_3$ , and had been formed by the rupture of the nitrogen ring, and not by addition at a carbon double linking. Further, the formation of dihalogenphenyldihydrothebaine occurs not smoothly, but with obvious structural changes, and offers therefore additional evidence of the absence of ethylenic linkages. On the other hand the reduction of thebaine with hydrogen in presence of metals of the platinum group led to the isolation of two hydrogenised bases of the formulæ,  $\text{C}_{24}\text{H}_{25}\text{NO}_2$  or  $\text{C}_{24}\text{H}_{25}\text{NO}_2$  and  $\text{C}_{24}\text{H}_{22}\text{NO}_2$ . Both are tertiary bases; the former still contains two methoxyl groups, whilst the latter has only one and possesses also a ketonic character. The relation of these substances to thebaine and the bearing of the whole work on the structure of that alkaloid are discussed at length.—G. F. M.

*N-Demethylcodeine.* O. Diels and E. Fischer. Ber., 1916, 49, 1721—1724.

IN addition to the method of preparing N-demethylcodeine previously described (this J., 1914, 765), it can also be made from codeine oxide as follows: 4 grms. of the oxide is treated with a 10% solution of potassium bichromate, and after the initial effervescence has subsided, the mixture is heated on the water-bath until all the formaldehyde produced has disappeared. It is then cooled and sufficient alcohol added to dissolve the brown flocculent precipitate and to separate inorganic compounds. After centrifuging, the liquid is decanted, evaporated on the water-bath, and the residue triturated with hydrochloric acid. The codeine derivative is thus obtained as a

crystalline mass, which should be crystallised from 50% alcohol. The "codeine-oxide-sulphonic acid hydrate" of Freund and Speyer (Ber., 1911, 44, 2339) is identical with N-demethylcodeine. —E. H. T.

**Picrotoxin**; The decomposition of — with methyl alcoholic potassium hydroxide; and picrotoxinic acid. P. Hermann and H. Wächter. Ber., 1916, 49, 1354—1567. (See also this J., 1916, 864.)

By treatment in the cold with methyl alcoholic potassium hydroxide, picrotoxin was resolved into the potassium salt of  $\beta$ -picrotoxinic acid (9.5%), the mono-methyl ester of picrotoxinindiacarboxylic acid (16%), and the methyl esters of picrotoxinic acid and  $\alpha$ -picrotoxinic acid, which on saponification gave picrotoxinic acid,  $C_{15}H_{18}O_8$ , in 41% yield,  $\alpha$ -picrotoxinic acid,  $C_{15}H_{18}O_8$ , in 17.5% yield, and picrotinolactone  $C_{15}H_{18}O_7$  (7.8%).  $\alpha$ -Picrotoxinic acid bears to picrotoxinic acid the relation of a hydroxy acid to the corresponding unsaturated acid, and by the ozone oxidation method an attempt was made to determine the position of the double bond in the latter substance. The results indicate the presence of an end methylene group in picrotoxinic acid, and that the oxidation to picrotoxinic acid follows the scheme:

$$CH_2 : C(C_6H_5, O_2) : CO_2H \rightarrow H.COOH + CO(C_6H_5, O_2) : CO_2H. \quad \text{—G. F. M.}$$

**Saponin from the epicarp of *Sapindus mukurosi*.** Y. Asahina and T. Shimidzu. Yakugakuzasshi, 1916, No. 410. J. Pharm. Chim., 1916, 14, 188—190.

The saponin of *Sapindus mukurosi* appears to be present in the form of a sodium or potassium salt, from which it is liberated by the action of acid. It was isolated as a white amorphous powder, which gives a yellowish-pink colour, changing to reddish-violet, with sulphuric acid. A solution in acetic anhydride yields a reddish-violet colour with a few drops of sulphuric acid. The saponin is insoluble in chloroform, ether, acetone, and light petroleum spirit, but soluble in ethyl and methyl alcohol. It is almost insoluble in water. If a little sodium bicarbonate solution is added to a suspension of the saponin in water, the saponin dissolves, forming a solution which lathers abundantly, and possesses to a marked degree the property of hemolysis. An aqueous solution of the saponin does not reduce Fehling's solution, but does so if previously boiled with dilute acids. It is dextro-rotatory ( $[\alpha]_D^{20} = +13.28^\circ$  in alcohol). It contains 63.02 to 63.45% of carbon and 8.21 to 8.49% of hydrogen, and determinations of its molecular weight gave values of 772, 811, and 820. Hydrolysis with 3% sulphuric acid, or better with alcoholic hydrochloric acid, produces *d*-arabinose and a saponin. The latter substance, having the formula  $C_{41}H_{78}O_{13}$ , crystallises from alcohol in small, tabular, colourless and tasteless crystals, of m.p.  $319^\circ C$ . It is insoluble in water, ether, chloroform, light petroleum spirit, or acetone, slightly soluble in ethyl or methyl alcohol, and very soluble in alcoholic potash. It gives the same colour reactions as the saponin. The authors suggest that the relation between saponin, saponin, and arabinose is given by the equation:

$$C_{41}H_{78}O_{13} + 2H_2O = C_{41}H_{78}O_{12} + 2(C_6H_{12}O_5). \quad \text{—F. Sp.}$$

**Betel vine leaves; Chemistry, physiology, and commercial bleaching of —.** H. H. Mann and V. G. Patwardhan. Mem. Dep. Agric. India, 1916, 4, 281—322. (See also this J., 1907, 1293; 1913, 922.)

COMMERCIAL betel-vine leaves from *Piper Betle*, intended for chewing, are usually mature or over-mature leaves which have not become brittle. In growing leaves which are not yet mature, the

starch, non-reducing sugars, and nitrates increase in amount during the day, whilst the reducing sugars, which form two-thirds of the total sugars, and the tannin and essential oil remain fairly constant throughout the day. In over-mature leaves the proportion of reducing sugars is very much smaller, whilst the non-reducing sugars are fairly constant and are present in by far the larger amount. A leaf for chewing should contain little starch and reducing sugars but a high proportion of sucrose. The most important factor in determining the value of the leaf is the amount and particularly the nature, of the essential oil present. The amount of essential oil increases very largely as the leaf becomes more suitable for use and declines when the leaf is over-mature. The essential oil of betel leaf (*pan* oil) consists essentially of phenols and terpene-like substances, the relative proportions of which vary in different varieties of leaves, the proportion of phenols being higher the more esteemed the quality of the leaf. The proportion of phenols in the oil from light green unbleached leaves varies from 42% (Poona green leaves) to 70% (Ramtek *Kapuri* leaves) and in dark-green leaves from 39% to 45%. Bleaching of betel-vine leaves increases the total amount of essential oil and also the proportion of phenols contained in the oil. The phenols consist chiefly of eugenol, mixed with a small amount of betel-phenol (chavibetol, 1-allyl-3-methoxy-4-hydroxybenzene), but no chavicol is present. An investigation into the method of bleaching betel leaves showed that (1) the bleaching must be carried out in absence of light, (2) the atmosphere in contact with the leaves must be sufficiently saturated with moisture to prevent the slightest drying of the leaves but must not contain more moisture than this, otherwise rotting ensues, (3) bleaching can be effected more rapidly and uniformly, with less loss, by rotting at  $29^\circ C$ . to  $33^\circ C$ . whilst temperatures above  $35^\circ C$ . are injurious and below  $24^\circ C$ . are useless. If bleaching is carried out beyond the stage when the leaves are yellowish-white the amount of essential oil and the quality of the leaves rapidly decline.—T. C.

**Hydrogenation of heterocyclic compounds. Catalytic hydrogenation. XII.** A. Skita and W. Brunner. Ber., 1916, 49, 1597—1603.

Pyridine was readily reduced to piperidine in dilute hydrochloric acid solution by hydrogen in presence of colloidal platinum. Traces of pentane were produced at the same time. The hydrogenation of  $\alpha$ -picoline,  $\alpha$ -lutidine, and 2,4,5-collidine proceeded with greater difficulty, but good results were obtained in acetic acid solution at  $25^\circ$ — $45^\circ C$ . under an excess pressure of 3 atm.  $\alpha$ -Phenylquinolinecarboxylic acid was reduced to tetrahydrophenylquinolinecarboxylic acid when treated in dilute glacial acetic acid solution at  $50^\circ$ — $60^\circ C$ . with hydrogen under an excess pressure of 1 atm., in presence of the platinum catalyst, whilst the decahydro-compound was obtained by working under a pressure of 3 atm., and using a larger quantity of catalyst. The tetrahydro-compound is crystalline and melts at  $218^\circ C$ , whilst the decahydro-derivative is amorphous, melting at  $330^\circ C$ . (with decomp.). The hydrogenation of the cinchona alkaloids, although presenting greater difficulty, was also effected. Thus quinine, or dihydroquinine, absorbed 3 or 6 mols. of hydrogen according to the duration of treatment, being converted into hexahydro-cinchonidine, m.p.  $206^\circ C$ , and dodecahydro-cinchonidine, m.p.  $104^\circ C$ . The same hexahydro-cinchonidine was also obtained by catalytic reduction of dihydrocinchonidine. Similarly by the hydrogenation of quinidine and cinchonine a hexahydrocinchonine of the formula  $C_{19}H_{28}N_2O$ , m.p.  $241^\circ C$ , was obtained.—G. F. M.

*Cholesterol into coprosterol; Conversion of* —. A. Windaus. Ber., 1916, 49, 1724—1734. (See this J., 1915, 198.)

By the reduction of cholesterol with hydrogen in presence of nickel, a new product,  $\gamma$ -cholestanol, was obtained, which has the same melting point and rotatory power as  $\beta$ -cholestanol but differs from it in crystallising from dilute alcohol without water of crystallisation. It was proved to be an addition compound of several hydrogenised cholesterol, and from it pseudo-coprosterol and  $\epsilon$ -cholestanol were obtained. The separation of these compounds proved extremely difficult, but was eventually effected by boiling with sodium amylate and amyl alcohol, precipitating with digitonin, and repeating the operation. In this way a filtrate was obtained containing practically pure pseudo-coprosterol. As the last named can be easily converted into coprosterol, the synthesis of the latter from cholesterol, which has hitherto only been effected by intestinal bacteria, is now possible by chemical means.—E. H. T.

*1,3-Diamines; Synthesis of* — by reduction of 2-mercapto-6-oxypyrimidines. T. B. Johnson and A. W. Joyce. J. Amer. Chem. Soc., 1916, 38, 1854—1860.

THE reduction of 6-oxypyrimidine-2-mercaptan derivatives by sodium and alcohol has been found to furnish a practical method for the synthesis of the corresponding 1,3-diamines, and the authors describe the preparation in this way of trimethylenediamine from 6-oxypyrimidine-2-methylmercaptan and from 5-ethoxy-6-oxypyrimidine-2-ethylmercaptan, of diaminobutane from 4-methyl-6-oxypyrimidine-2-ethylmercaptan and from 2-thio-4-methyl-6-oxypyrimidine, of 1,3-diaminoisobutane from 5-methyl-6-oxypyrimidine-2-ethylmercaptan, of 1-amino-3-methylamino-propane from 1-methyl-6-oxypyrimidine-2-ethylmercaptan, and of 1-methylamino-3-aminobutane from 1,4-dimethyl-6-oxypyrimidine-2-ethylmercaptan. The oxypyrimidine derivatives are easily synthesised, and it is possible to prepare from them mono-alkylated diamines difficult to obtain by any other method.—A. S.

*Acetylsalicylic acid; Physical and chemical tests for* —. D. E. Tsakalotos. J. Pharm. Chim., 1916, 14, 174—177.

ACETYSALICYLIC acid when heated just to its melting point on an object glass, and allowed to solidify, crystallises in concentric rings. If heated to a somewhat higher temperature solidification is slow and a vitreous mass is formed. When acetylsalicylic acid is maintained in a fused condition acetic acid is evolved and salicylsalicylic acid is formed. For this reason an accurate determination of its melting point is impossible since this depends on the rate of heating. A solution of pure acetylsalicylic acid prepared rapidly by dissolving in alcohol and adding water, gives at first no reaction with dilute ferric chloride. If the solution stands for some time before being tested, a violet coloration is produced. If the acid is heated just to its melting point and then dissolved, it gives an immediate intense violet coloration with ferric chloride. If it is heated above its melting point and then dissolved in alcohol, water precipitates salicylsalicylic acid and ferric chloride gives a pale violet colour. Self's vanadium reagent for salicylic acid (this J., 1915, 511) is more simply prepared by dissolving a little ammonium vanadate in concentrated sulphuric acid, and adding water until the intensity of the orange colour begins to diminish; the formaldehyde may be omitted. Solid acetylsalicylic acid with this reagent gives no result at first, but after a few instants a yellowish-green colour develops, changing to an intense green. If the acid is previously heated to its melting

point, it gives an intense green colour at once, while if previously heated above its melting point, a deep green colour changing instantly to brown is observed.—F. SP.

*Arseno-compounds; Aromatic* —. XI. *Mixed arsono-compounds*. P. Karrer. Ber., 1916, 49, 1648—1650.

UNSYMMETRICAL arsono-compounds are obtained by the interaction in solution of two symmetrical compounds according to the equation:—

$R.As : AsR + R'.As + AsR' = 2R.As : AsR'$ . Thus when 3,4,5,3',4',5'-hexa-aminoarsenobenzene hydrochloride and 3,3'-diamino-4,4'-dihydroxyarsenobenzene hydrochloride are rapidly heated to 80° C. in aqueous solution, and a large excess of hydrochloric acid (sp.gr. 1.12) added, the mixed arsono-compound of the formula  $(OH)(NH_2)C_6H_3.As : As-C_6H_3(NH_2)_2.3HCl$ , is precipitated in bright yellow flakes. The mixed arsono-compound obtained in a similar way from hexa-aminoarsenobenzene and tetra-amino-dimethyldiaminoarsenobenzene is also described.—G. F. M.

*Arsenobenzene derivatives; Causes of the injurious effects observed after the injection of* —. J. Danysz. Comptes rend., 1916, 163, 246—248.

THE injurious effects sometimes produced by the injection of products containing the arsenobenzene group (e.g. neo- and novo-salvarsan) are due to vaso-dilation and to the formation of a precipitate which clogs the capillaries. The mono- and disodium salts of the arsenobenzene derivatives are particularly liable to give precipitates in the presence of mineral salts, including sodium chloride, but the precipitation may be retarded or prevented by the presence of blood serum, sugar, or glycerol. Prolonged treatment with very dilute solutions is recommended. The di-sodium salts of the products are more active, and at the same time safer, than the neutral products. It is pointed out that the formation of a precipitate, manifested by the appearance of unpleasant symptoms within 6 hours after the injection, is an essential factor in the therapeutical efficiency of the products.—W. P. S.

*Hydrolysis of phenyl ethers and esters by means of the hydrochlorides of aromatic bases. Preparation of anilides and their homologues*. Klemenc. See III.

*Behaviour of chromous salts towards acetylene, and the reducing action of salts of divalent chromium*. Traube and Passarge. See VII.

*Action of hydrogen sulphide on dextrose*. Schneider. See XVII.

*Methylheptenone as an insecticide*. See XIXb.

*Petrographic microscope in analysis*. Wright. See XXIII.

#### PATENTS.

*Anhydrides of fatty acids; Process of manufacturing* —. K. Goldschmidt and F. Spitzer, Essen, Germany, Assignors to General Chemical Co., New York. U.S. Pat. 1,195,205, Aug. 22, 1916. Date of appl., Oct. 29, 1909.

SEE Eng. Pat. 25,433 of 1908; this J., 1910, 112.

*Anhydrides; Manufacture of organic acid* —. F. W. Jahn, Assignor to General Chemical Co., New York. U.S. Pat. 1,195,227, Aug. 22, 1916. Date of appl., Mar. 27, 1909.

SEE Eng. Pat. 5939 of 1910; this J., 1910, 1227.

*Nicotine; Process of extracting* — from green or uncured tobacco. H. Villiers-Stuart, Lismore, Ireland. U.S. Pat. 1,196,184, Aug. 29, 1916. Date of appl., May 9, 1913.

SEE Eng. Pat. 20,347 of 1912; this J., 1913, 924.

*Unsaturated hydrocarbons containing the conjugated bond; Process for the purification of* —. F. E. Matthews, Blackheath, and E. H. Strange. London. U.S. Pat. 1,196,259, Aug. 29, 1916. Date of appl., Mar. 16, 1915.

SEE Eng. Pat. 6897 of 1914; this J., 1915, 635.

*Unsaturated hydrocarbons; Process for purifying* —. F. E. Matthews and E. H. Strange. Fr. Pat. 477,983, Mar. 11, 1915.

SEE Eng. Pat. 6897 of 1914; this J., 1915, 635.

*Menthyl methylsalicylate; Manufacture of* —. New York Salesthyll Corporation. Fr. Pat. 478,102, Mar. 20, 1915.

SEE U.S. Pat. 1,133,832 of 1915; this J., 1915, 575.

*Benziminazoles containing the ethylamino group, and their preparation.* D. Maron. Fr. Pat. 478,299, Apr. 6, 1915.

SEE Eng. Pat. 1752 of 1915; this J., 1916, 197.

*4-N-Alkylnitrosaminoaryl-1-arsenic acids; Preparation of* —. Les Etabl. Poulenc frères, and K. J. Oechslin. Fr. Pat. 479,646, Dec. 28, 1914.

SEE Eng. Pat. 22,522 of 1914; this J., 1916, 557.

## **XXI.—PHOTOGRAPHIC MATERIALS AND PROCESSES.**

*Collodion silver bromide emulsions.* Lüppo-Cramer. Koll.-Zeits., 1916, 18, 18—20. Chem.-Zeit., 1916, 40, Rep., 304.

UNLIKE gelatin emulsions in which an increase in size of grain is accompanied by an increase in sensitiveness, collodion emulsions lose sensitiveness with increase of size of grain if digested for some hours with an excess of ammonium bromide. It is advisable therefore to work with as small an excess of bromide as possible and to wash the emulsions soon after preparation.—B. V. S.

*Antimony toning of developed pictures.* L. Strasser. Phot. Rundsch., 1916, 53, 33—35. Chem.-Zeit., 1916, 40, Rep., 304.

By treatment of a bleached silver print with a 0.5% solution of Schlippe's salt (sodium thioantimonate) a stable red-brown tone is obtained with no alteration of gradation. Simultaneous or subsequent sulphide toning gives a colder brown tone.—B. V. S.

*Petrographic microscope in analysis.* Wright. See XXIII.

### **PATENTS.**

*Photographic transfer processes.* F. W. Kent, Clapham, and T. P. Middleton, Farnham. Eng. Pat. 12,091, Aug. 21, 1915.

THE process described in Eng. Pat. 29,616 of 1912 (this J., 1914, 221) is extended and modified. Paper to be used as base for a transfer process is saturated with paraffin wax and the surface buffed with a rotary brush while the wax is still soft. One side of the paper is coated with a substratum solution of pyroxylin and then with a sensitised gelatin emulsion. By dissolving the pyroxylin in a mixture of alcohol and ethyl acetate or similar solvent containing a little water, a porous friable film is obtained which is sufficiently adherent to retain the emulsion on the waxed paper, but allows easy stripping. A description is given of an apparatus for waxing, buffing, substratum-coating, and emulsion-coating in a continuous operation. The surface to which the print is to be transferred is preferably prepared with a solution of gelatin, fish-glue, or similar water-soluble cement, instead of with a solution of resin or rubber or similar substance as explained in the first patent.—B. V. S.

*Colour photography.* A. N. Pierman, Newark, N.J. U.S. Pat. 1,196,718, Aug. 20, 1916. Date of appl., Apr. 8, 1908.

A MULTICOLOUR screen is composed of flexible coloured strands woven together in a regular pattern and embedded in a thin flexible transparent or translucent ribbon by soaking the screen in a suitable solution, e.g., a collodion solution, and drying off. The composite film is coated with sensitive emulsion.—B. V. S.

*Röntgen photography; Sensitive plate for — and process of making the same.* H. Arnold, Charlottenburg, and M. Levy-Dorn, Berlin, Germany. U.S. Pat. 1,195,432, Aug. 22, 1916. Date of appl., Mar. 1, 1915.

SEE Eng. Pat. 2243 of 1915; this J., 1916, 386.

*Photographs in colour and method of making the same.* J. G. Capstaff, Assignor to Eastman Kodak Co., Rochester, N.Y. U.S. Pat. 1,196,080, Aug. 29, 1916. Date of appl., Sept. 21, 1914.

SEE Eng. Pat. 13,430 of 1915; this J., 1916, 907.

*Coloured images; Process for obtaining* —. Kinemacolor Co. of America. Fr. Pat. 478,011, Mar. 13, 1915.

SEE Eng. Pat. 3666 of 1915; this J., 1916, 73.

*Screens for colour photography and photography in general.* J. Rheinberg. Fr. Pat. 478,117, Mar. 22, 1915.

SEE Eng. Pat. 9929 of 1914; this J., 1915, 637.

*Photography in colours.* J. E. Thornton. Fr. Pat. 478,928, June 5, 1915.

SEE Eng. Pat. 13,711 of 1914; this J., 1915, 818.

*Photographic images in colours; Production of* —. P. D. Brewster. Fr. Pat. 479,160, Jan. 21, 1915.

SEE Eng. Pat. 1073 of 1915; this J., 1916, 329.

*Photographic developer.* T. J. Brewster. Fr. Pat. 479,665, Sept. 4, 1915.

SEE Eng. Pat. 9331 of 1915; this J., 1916, 907.

## **XXIII.—ANALYSIS.**

*Petrographic microscope in analysis.* F. E. Wright. J. Amer. Chem. Soc., 1916, 38, 1647—1658.

IT is possible with the aid of the petrographic microscope to measure readily, and with sufficient accuracy, the optical constants of crystal grains measuring only 0.01 mm. in diameter, and the author discusses briefly the application of the instrument to chemical problems. It is possible, for example, to identify any one of the pentose- and hexose-osazones by means of their optical constants, even though only a few milligrams of substance is available. In the identification of alkaloids, also, where chemical methods are unsatisfactory or difficult to apply, the petrographic microscope should prove of value. Other applications mentioned include the examination of baking and cleaning powders, abrasives, paints, fertilisers, cements, drugs, sugars, salt, and photographic developers.—A. S.

*Hydrogen ions; Use of solutions of borax and boric acid in the colorimetric determination of the concentration of — in sea water.* S. Palitzsch. Comptes rend. Trav. Lab. Carlsberg, 1916, 11, 199—211.

SOLUTIONS of known concentration of hydrogen ions, to serve as standards in colorimetry, may be conveniently prepared from suitable proportions of boric acid and borax, both of which can be easily obtained sufficiently pure and stored for long periods, in the crystalline form, without

change. The author has studied in particular the preparation of solutions having  $pH$  between 7 and 9, for use in testing the reaction of sea water during an Arctic expedition. The values of  $pH$  for mixtures of an M/20 solution of borax and an M/5 solution of boric acid, in various proportions, are given, and also the "salt error" for quantities of sodium chloride up to 3.5% when phenolphthalein, naphtholphthalein (see this J., 1910, 1178), or neutral red is employed.—J. H. L.

*Metals of the copper-tin group; Electroanalytical method for determination and separation of —.*

E. P. Schoch, D. J. Brown, and T. E. Phipps. J. Amer. Chem. Soc., 1916, 38, 1660—1681.

ANTIMONY, bismuth, copper, lead, tin, and cadmium may be deposited quantitatively from hydrochloric acid electrolytes, if a suitable reducing agent, e.g., hydroxylamine hydrochloride, is present in the solution and oxides of nitrogen or nitric acid are absent, and the same electrolytes may be used to separate the metals mentioned from each other and from other metals of the copper-tin group by the graded potential method. The authors use the Sand-Fischer apparatus and electrodes (Sand, this J., 1907, 490; 1908, 963; Fischer, *Elektroanal. Schnellmethoden*), with a special clamp which allows either of the electrodes to be removed and replaced quickly without disturbing the other, and renders the apparatus more rigid, so that it is possible to rotate the stirrer at a speed of 800 revolutions per minute without loss of electrolyte by splashing. The electrolyte (150—200 c.c.) should be of such concentration as to give a deposit of at least 0.1 gm. of any constituent and a total for any single deposit not exceeding 0.67 gm., and 2 grms. of hydroxylamine hydrochloride is added to remove oxides of nitrogen and free chlorine. If arsenic is present, 3 grms. of hydroxylamine hydrochloride is added, and the arsenic is removed by distillation in a current of hydrogen chloride. Bismuth, copper, and antimony are deposited together with the minimum electromotive force, then tin and lead together, and subsequently cadmium. Detailed descriptions are given of the determination of tin; determination of copper; separation of copper from tin; determination of bismuth; determination of antimony; separation of antimony or bismuth from tin; determination of lead; simultaneous deposition of lead and tin, and their separation; separation of tin from cadmium; separation of copper from antimony; simultaneous deposition of copper and antimony in presence of lead; simultaneous deposition of copper, bismuth, and antimony in presence of tin or of tin and lead; separation of bismuth from antimony; simultaneous deposition of copper and bismuth in presence of antimony; separation of bismuth and copper by precipitation of the bismuth as phosphate.—A. S.

*Silver; Electroanalysis of — with solutions of silver chloride in ammonia.* E. P. Schoch and F. M. Crawford. J. Amer. Chem. Soc., 1916, 38, 1682—1683.

ABOUT 150 c.c. of solution containing from 0.16 to 0.59 gm. of silver in the form of chloride dissolved in excess of ammonia and 20 grms. of ammonium chloride is electrolysed in the apparatus described in the preceding abstract. An initial current of 0.35 ampère is used, corresponding to a potential difference of 1.1 volts between the electrodes, and the voltage is kept constant until the current drops to zero, and then allowed to rise gradually to 1.3—1.4 volts, and electrolysis continued for 25—30 mins. About 99.6% of the total silver is thus deposited; 3 grms. of crystallised oxalic acid is then added, the solution is made slightly acid to litmus by means of concentrated hydrochloric acid, and electrolysis continued for 20 mins. to deposit the last traces of silver.—A. S.

*Rapid method for determination of sulphur in coal gas.* Mylius and Hüttner. See IIA.

*Volumetric determination of hydrogen by oxidation with activated chlorate solution. Removal of carbon monoxide by means of mercuric chromate.* Hofmann. See IIA.

*Retardation by carbon monoxide of the oxidation of hydrogen in the chlorate pipette, a contribution to the knowledge of contact poisons.* Hofmann and Schibsted. See IIA.

*Sodium pyrogallate as a reagent for the determination of oxygen.* Shipley. See IIA.

*Detection of nickel in cobalt salts.* Middleton and Miller. See VII.

*Oxidation of manganous to manganic salts by nitrous acid.* Prandtl. See VII.

*Behaviour of chromous salts towards acetylene, and the reducing action of salts of divalent chromium.* Traube and Passarge. See VII.

*Use of diphenylglyoxime as indicator in volumetric determination of nickel in iron and steel by Frevet's method.* Kelly and Conant. See X.

*Volumetric determination of lead.* Waddell. See X.

*Examination of Chinese wood oil.* Browne. See XII.

*Chemical and microscopical examination of leather.* Seel and Sander. See XV.

*Determination of chromic oxide in chrome-tanned leather.* Lamb and Harvey. See XV.

*Benzoyldihydromethylketol-hydrazine, a new reagent for galactose.* Von Braun. See XVII.

*Comparison of the bacterial count with the sediment or dirt test of milk.* Campbell. See XIXA.

*Origin of the humin nitrogen formed by the acid hydrolysis of proteins. Hydrolysis in the presence of carbohydrates and of aldehydes.* Gortner. See XIXA.

*Analysis of mineral waters by volumetric methods. [Determination of magnesium.]* Jensen. See XIXB.

*Determination of thiosulphate sulphur in lime-sulphur solutions by iodine titration.* Blumenthal and Averitt. See XIXB.

*Physical and chemical tests for acetylsalicylic acid.* Tsakalotos. See XX.

#### PATENTS.

*Detecting and indicating the presence and proportion of a gas mixed with air or other gases; Apparatus for —.* H. R. Webster. Fr. Pat. 478,307, Apr. 13, 1915.

SEE Eng. Pat. 9196 of 1914; this J., 1915, 639.

*Apparatus for and method of measuring the plasticity of rubber and rubber mixings.* Eng. Pat. 15,438. See XIV.

#### Book Received.

GAS CHEMISTS' SUMMARY, 1915. By A. V. HENDRICKSON. Published by Walter King, 11, Bolt Court, Fleet Street, E.C. 216 pages. Price 3s. 6d.

THE appearance of this useful annual will be welcomed by all those interested in the chemistry of gaseous fuels. It is divided into chapters as follows.—I. Carbonisation. II. Condensation, washing, purification, naphthalene and cyanogen extraction. III. Tar and ammonia. IV. Oil and carburetted water-gas. V. Photometry and calorimetry. VI. Gaseous heating and ventilation. VII. Gas analysis. VIII. Tests. IX. Miscellaneous. A bibliography and subject and name indexes conclude the volume.

